



Analytical Methods for Graphite Tube Atomizers

User's Guide



Agilent Technologies

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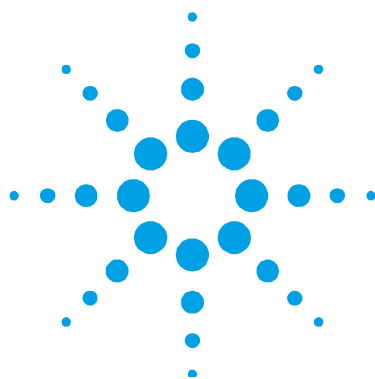
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1. Furnace Atomization

Graphite furnace atomic absorption (AA) has now gained a reputation in the field of analytical chemistry as a routine technique for the determination of very low levels of trace metals in a variety of sample types. This is in contrast to the situation several years ago when it was regarded more as a research accessory. The Zeeman background correction technique has further enhanced the quality of the results obtained from the graphite tube atomizer.

The generation of atoms by means of an electrically heated graphite furnace atomizer is a technique which is complementary to conventional flame AA, rather than a technique which replaces it. There are many analytical advantages of flame AA, but there are many trace metal analyses which are only possible by means of a graphite furnace atomizer. With these two techniques for the generation of ground state atoms, plus the vapor generation method for some selective elements, AA remains one of the most versatile yet specific analytical methods for the measurement of metals.

Flame Compared With Graphite Furnace Atomization

Flame systems for atomic absorption spectroscopy give excellent results, and they are simple, convenient and extremely useful. They permit rapid analytical measurement through a very simple sample introduction technique.

However, it is worth examining briefly the disadvantages of flame atomization which highlight the desirability of alternative atomization processes:

- The efficiency of pneumatic nebulizer/spray chamber systems is low; typically about 10%. Thus for every milliliter of solution aspirated, 0.9 mL is wasted and only 0.1 mL reaches the flame as a fine aerosol.
- For the amount of sample finally reaching the flame, the production of atoms in the ground state is governed by many variables such as the flame temperature, interactions between flame gases, matrix components and analyte, chemical interferences, and the extent to which the analyte molecular species are dissociated.
- The zone of the flame in which absorption actually occurs is only a small section of the whole flame. Effective absorption therefore depends on the fraction of ground state atoms present in the light path at any particular instant. The residence time of an atom within the light path is extremely short – typically 10^{-4} seconds – and depends on the velocity of the flame gases.
- The overall effect of (a), (b) and (c) is that the number of atoms contributing to the analytical signal is extremely small compared with the total amount of element aspirated. Therefore, the entire process is inefficient in terms of sample usage.
- Flame gases also produce distinct absorption and emission bands which can cause interference and background noise.

The advent of ‘flameless’ atomization, in particular the pyrolytic coated graphite tube furnace (or carbon rod type) atomizer, greatly reduced these physical and chemical limitations imposed by the flame atomization process.

- With the graphite atomizer, a discreet volume of sample solution is vaporized and wastage is virtually eliminated.
- Although the ground state atom population is still subject to interferences, they are of a different nature to those found in flame atomization but are amenable to control by proper choice of analytical conditions, and chemical pre-treatment.
- The graphite tube is in effect a confined furnace chamber where pulse vaporization of the element is achieved by raising the temperature with a programmed sequence of electrical power. Consequently, a dense population of ground state atoms is produced for a longer time interval in contrast to the low atom density and short residence time of the flame.

The overall effect is that the analytical sensitivity is greatly enhanced using graphite atomization. The application of ‘furnace’ techniques in analytical atomic spectroscopy can be attributed L'vov and Massmann who independently developed the technique (1, 2).

Advantages of Furnace Atomization

Flame AA systems are subject to sensitivity limitations which restrict the analytical scope of flame methods. Furnace atomization will overcome these limitations and provide three important advantages:

Firstly, sensitivity is better. Graphite furnace atomizer methods are typically 100 times more sensitive than flame methods for most elements in a wide range of samples, i.e. for a given concentration the signal will be about 100 times that obtained by flame atomization. For example, Figures 1 and 2 show the determination of molybdenum by flame and furnace methods.

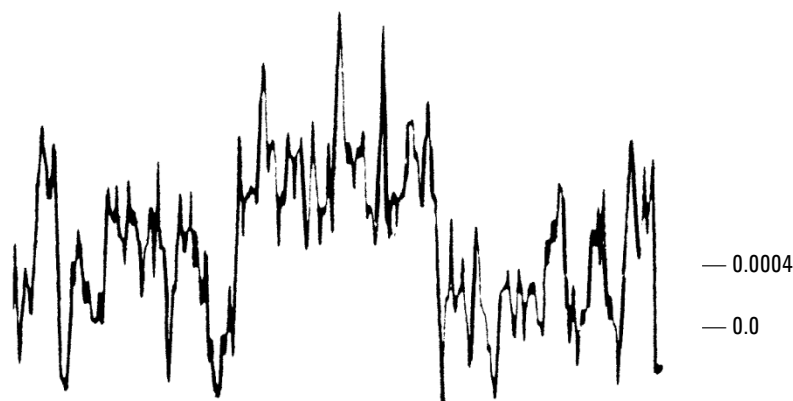


Figure 1. Molybdenum determination by flame AA (30 µg Mo/L). Nitrous oxide-acetylene flame, scale expansion 25X.

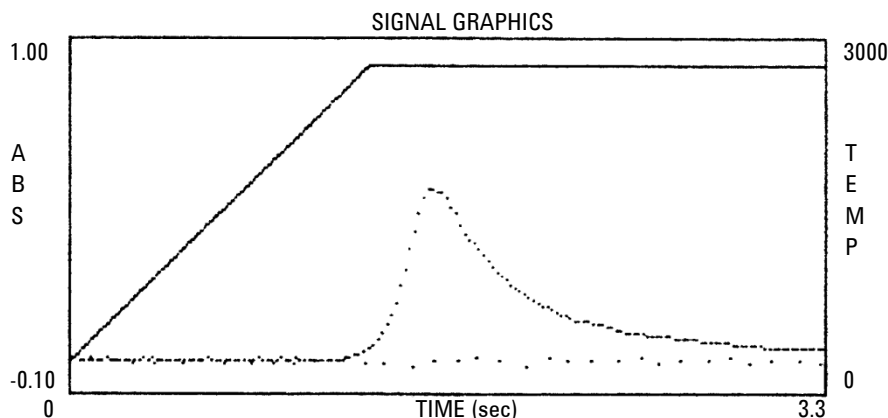


Figure 2. Molybdenum determination by Zeeman graphite furnace (30 μL ; 30 ng/mL).

Secondly, less sample is needed. Determinations typically can be carried out with only 5 μL (0.005 mL) of sample; up to 100 μL (0.1 mL) may be accepted. Flame methods normally require about 5 mL.

Thirdly, sample preparation can be simplified. Many samples such as concentrated acids, viscous liquids, organic solvents and liquids with high dissolved solids can be analyzed directly on the graphite furnace atomizer. The higher sensitivity of the method means that solvent extraction or preconcentration procedures may be avoided; sample preparation and handling can be minimized.

However, the graphite furnace atomizer is not recommended if:

- The sample is already in a liquid form and the concentration of the analyte permits a simple analysis by flame AA.
- Certain refractory elements such as tungsten, tantalum or zirconium are to be determined. Some elements cannot be easily atomized by the graphite furnace, and flame AA remains the best technique.

Furnace atomization is a single measurement analytical technique. That is, a fixed volume of sample is analyzed at one time, in contrast to flame atomization where the sample is continuously aspirated and many measurements can be taken during the aspiration period. The need for background correction is especially important with graphite furnaces, in contrast to most flame analyses.

Although there are different approaches to the construction of high temperature furnaces, they are all designed to perform the same function – generate a population of free atoms so that atomic absorption can be measured. This is generally achieved in three stages:

- 1** A DRYING stage during which the solvent is removed from the sample in the furnace.
- 2** An ASHING stage which removes organic molecules or inorganic material.
- 3** An ATOMIZATION stage in which free atoms are generated within a confined zone. The absorption signal produced in the atomization stage is a sharp peak, the height (or area) of which can be related to the amount of analyte element present.

There are certain limitations with this three stage analytical program which have been overcome with more flexible programs on modern instrumentation.

Development of Agilent's Graphite Furnace Atomizers

The first carbon rod atomizer to be produced commercially was developed and marketed by Varian in 1970. This device (known as the Model 61) was largely patterned after the device described by West and Williams in 1969 (3). The workhead consisted of two water-cooled terminal blocks which supported a single electrode. The original filament, often referred to as the 'West' rod, contained a small indent in the centre of the rod where samples were evaporated, ashed and atomized. An important point to note with this design is that the atoms are observed in an open region above the hot graphite where they were originally atomized. This gave rise to severe chemical interferences for many elements. Later developments showed that, if hydrogen was mixed with the inert sheath gas, these interferences could be minimized because of the ensuing hydrogen diffusion flame. The device, though limited in many respects, still offered unique applications capabilities.

At about the time that Varian's carbon rod atomizer made its first appearance, other commercial graphite furnace atomizers were being developed in Europe and America. The most interesting of these was the heated graphite atomizer based on Massmann's work with the graphite tube furnace (2). The heated tube concept employed in the Massmann design confined the atoms, thereby increasing their residence time in the optical path and decreasing chemical interference problems when compared with the West design.

The next step by Varian (4, 5) was to combine the virtues of the West rod (compactness, low power consumption, speed of operation) with those of the Massmann furnace (wide range of elements, freedom from chemical interferences). A miniature furnace approach was developed by changing the electrode design. This new design was called the 'Mini-Massmann' rod. It consisted of a graphite rod 5 mm in diameter with a transverse hole of 1.5 mm diameter. This design produced in essence a miniature furnace. This furnace could accommodate volumes only to a maximum of 2 μL ; ideally 0.5 or 1 μL . Samples were injected with a metal tipped microsyringe. The small size of the furnace required that the operator be skilled for its successful operation.

Reproducibility problems were also encountered if the metal syringe tip gouged the internal part of the cavity. Elements which readily form refractory carbides were impossible to analyze and memory effects were common as samples tended to soak into the graphite furnace walls.

With the introduction of the Model 63 carbon rod atomizer in 1972, many of these early problems which limited the use of 'flameless' atomizers for the routine analysis of samples were eliminated (6). The next development in furnace atomization, the CRA-90 carbon rod atomizer maintained the elegance and simplicity of the Model 63, but offered better power control, increased cooling capability to speed analyses, and temperature readout capability for operator convenience (7).

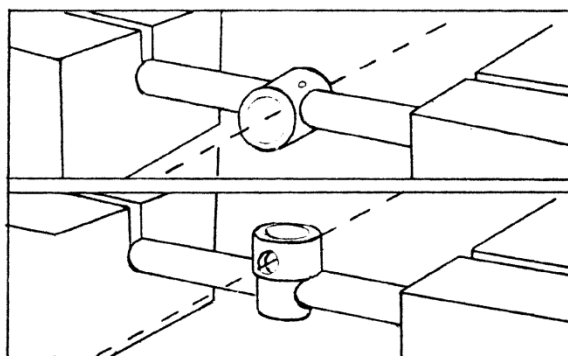


Figure 3. CRA-90 tube and cup furnace

Two types of furnace atomizer were available – the tube and the cup (see Figure 3). The tube furnace is generally more sensitive; the cup furnace allows the use of powdered or solid samples.

The temperature is raised because of the heating effect of the contact resistance between the cup or tube atomizer and the electrodes.

To protect the incandescent graphite from excessive corrosion, there is an upward flow of inert gas (argon or nitrogen) which surrounds the heated graphite. This serves not only to protect the pyrolytic coating, but also sweeps away any ashing products from the light path.

In 1981, Varian introduced a new graphite furnace featuring a fully enclosed graphite tube with longitudinal resistive heating. It was designated the GTA-95 and represented a major step forward in furnace AA technology. Further improvements were made with the later introduction of the GTA-96.

Varian have developed the Zeeman graphite tube atomizer based upon the GTA-96 and the SpectrAA series instrumentation. The following performance features apply:

- Improved quality of background correction.
- Large sample volume capability for improved detection limits and ease of sample introduction.
- Multi-step temperature program to provide exacting drying, ashing and atomization temperatures (and temperature ramps) to suit the application.
- Ability to provide a second atomization during one analysis in order to reduce memory or remove residual contaminants, before the next sample is added.
- Inert gas flow can be set (from 0-3 L/min) at any time during the analytical program to permit ashing or to enhance the atomization signal.
- An alternative gas may be used at any preselected time during the program, to facilitate ashing or to enhance the atomization signal.
- Simple, routine preparation of standard additions, and addition of chemical modifiers when coupled to the autosampler.
- Ability to accommodate a pyrolytic platform.

A cross-section of the furnace appears in Figure 4 on Page 16.

The graphite contact cones are held in a water-cooled copper block, and have a small contact area with the pyrolytic coated graphite tube. The graphite tube is resistively heated by the passage of a high current (at low voltage) through the tube. Inert gas (normally argon or nitrogen) flows through the graphite cones from each end and protects both the inside and outside of the pyrolytic coated graphite tube from rapid oxidation. The inert gas flow can be programmed (from 0-3 L/min) in order to provide the desired result. The magnet is placed about the graphite tube as shown in Figure 4.

The ability to use an alternative gas during the program allows considerable flexibility in experimentation with gases to aid the ashing of samples, or to enhance the sensitivity.

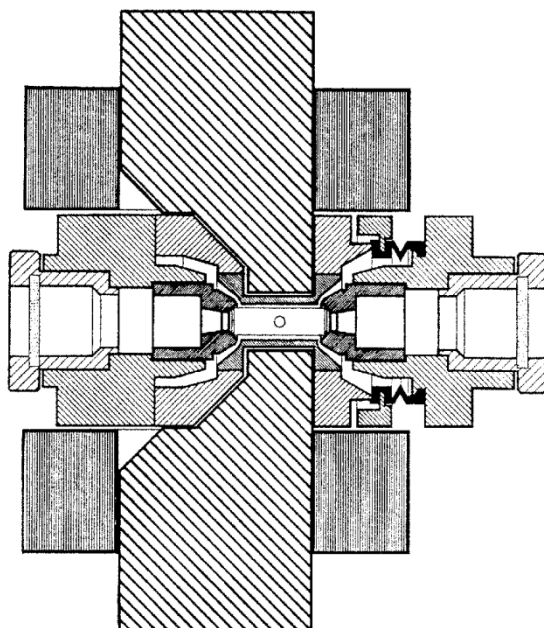


Figure 4. Cross section of the Zeeman graphite furnace

Pyrolytic Graphite Coatings

The pyrolytic coating on the graphite tube is a vital component of a successful analysis. The thickness of this coating is about $30\ \mu\text{m}$ ($30 \times 10^{-4}\ \text{cm}$ or $0.0012\ \text{in.}$). Figure 5 shows a cross section of graphite substrate material with its pyrolytic coating.

In the manufacturing process pyrolytic graphite is deposited on the substrate graphite from the vapor phase after thermal decomposition of a simple hydrocarbon such as methane under low pressure. As this deposition proceeds, a dense, hard layer of pyrolytic carbon is built up over the substrate graphite. The crystals of the pyrolytic graphite lie virtually parallel to the surface and it is highly anisotropic, both electrically and thermally. The graphite tube atomizer tubes are supplied coated in this manner.

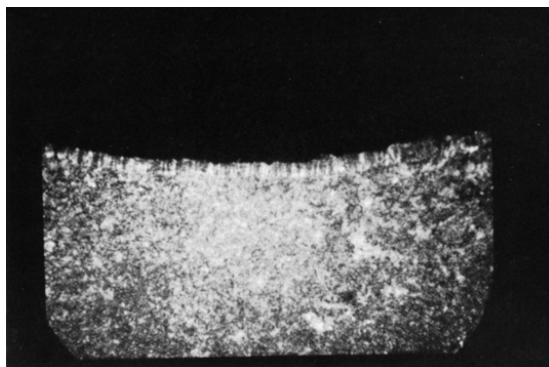


Figure 5. Photomicrograph of pyrolytic coating. Photomicrograph by courtesy of Dr D. Lynch, CSIRO, Melbourne, Australia.

The advantages of this coating for atomic absorption analysis are:

- The coating is relatively impermeable to hot gases (or atoms).
- It is more resistant to oxidation than normal graphite.
- It is unreactive chemically, and the tendency for some refractory elements to form carbides is significantly reduced, e.g. with vanadium, titanium, molybdenum.

Pyrolytic graphite coating on the tube ensures that the lifetime is good and the analytical sensitivity is enhanced for several elements.

Pyrolytic graphite remains a unique material with many desirable properties for graphite furnace AA. Certain metal coatings on the graphite substrate, however, can enhance the sensitivity for some elements (8-12). This will be discussed in more detail under the title 'Mechanism of Atom Formation'. Whereas the graphite atomizers as supplied by Varian are pyrolytic coated, there are reports of its deposition onto a graphite tube in situ by heating the furnace in the presence of an argon-methane mixture (13). At a temperature of about 2200 °C, methane decomposes to deposit as pyrolytic graphite on the substrate material. The quality of such a coating will depend entirely on parameters such as gas flows, temperature and the duration of the process, etc.

Graphite Tube Types

Two types of tubes are available. The pyrolytic coated partitioned tube is the one which is normally used for analytical work which does not require the pyrolytic platform.

A ridge in the partitioned tube confines the liquid sample to the central part of the tube and enables even large volumes of organic solvents to be dried reproducibly (See Figure 6). It is also especially suitable for high concentrations of acids (such as nitric) which would otherwise tend to spread along the tube surface. The partitioned tube cannot be used with the platform.

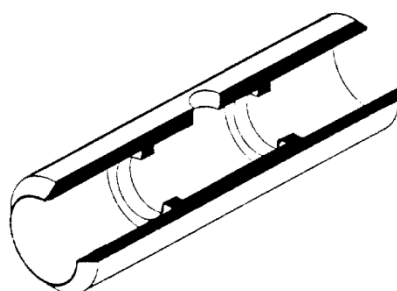


Figure 6. Cross sectional view of the partitioned graphite tube

Pyrolytic Platform

The other type of tube is the pyrolytic coated plateau tube which is required for the pyrolytic platform (see Figure 7). This tube is not normally recommended for use alone (the partitioned tube is preferred).

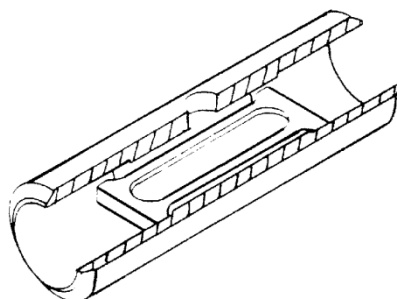


Figure 7. Graphite tube with platform

The pyrolytic platform is a single piece of solid pyrolytic graphite which contains a central depression to enable it to contain liquid samples up to about 40 µL. The platform has lobes at the ends which locate it inside the plateau type tube (See Figure 7). There is minimal physical contact between the tube and the platform.

The effect of the platform is to delay the vaporization of the sample until the graphite tube has reached a stable (high) temperature. The high temperature environment will assist in minimizing vapor-phase interferences (see also Chapter Three).

There are a number of references on the benefits and applications of pyrolytic platforms of Varian GTA graphite furnaces. (300- 305)

Elemental Capabilities of Furnace Atomization

Furnace atomization is not applicable to all 67 elements which can be analyzed by flame atomization.

It would appear that the inability of furnace atomization to determine certain elements is not related to any temperature limitation. It is more closely related to the chemical decomposition reactions which precede atom formation. Chemical species which exist in flames are quite different from those which are likely to be present inside a heated graphite furnace. Flames contain reactive radicals, e.g. C, C₂, CH, H₂O, CN, NH. The presence of these reactive species in the flame strongly enhances the dissociation of metal compounds. A graphite furnace does not contain such a variety of chemical species and consequently the dissociation and atomization of certain metals is not possible.

A large number of elements form stable carbides in the presence of graphite at high temperatures. Tungsten, for example, will form a carbide at about 2500 °C. This carbide formation inhibits the decomposition process and thus makes it difficult to determine those elements which form such refractory carbides.

There are of course various degrees of difficulty of analysis.

Those elements classed as not successfully analyzed by furnace atomization characteristically exhibit a high memory, i.e. there is significant residual signal from a second atomization without further sample addition. This percentage memory would be as high as 90% for elements such as tungsten.

Those elements classed as successfully analyzed by furnace atomization would typically have a memory of less than 10%. Many elements of course exhibit no memory at all.

Among those high temperature refractory elements which can be analyzed by the graphite tube atomizer are boron, dysprosium, erbium, molybdenum, silicon, titanium and vanadium.

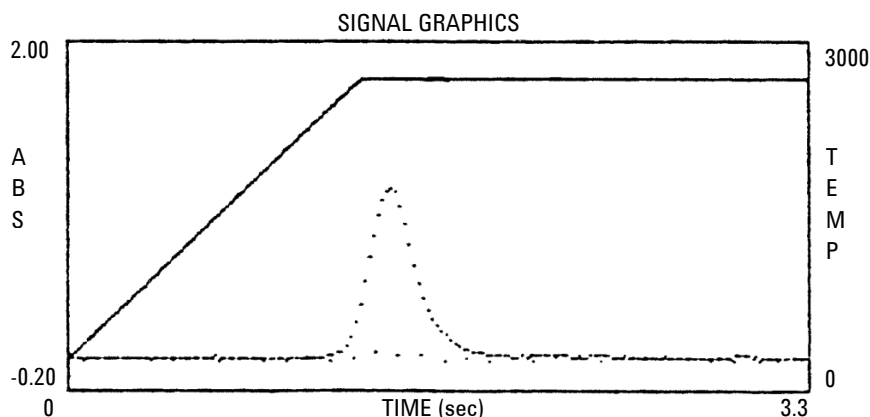


Figure 8. Signal graphics trace for the determination of aqueous silicon. The Zeeman background trace appears at the base of the silicon peak. Temperature profile is displayed.

Figure 8 shows a graphics trace for the determination of aqueous silicon. This signal represents a 12 μL sample of 400 ng/mL silicon, atomized at 2700 $^{\circ}\text{C}$.

Remember that with elements which require a high atomize temperature (around 2700 $^{\circ}\text{C}$) the lifetime of the graphite components may be relatively short (about 500 firings). With the elements which require a low atomize temperature (around 1800 $^{\circ}\text{C}$) many more atomizations are possible.

Whereas these tube lifetimes apply to simple aqueous solutions, the lifetime would be severely reduced if the sample contains high concentrations of certain compounds such as strongly oxidizing acids.

Mechanism of Atom Formation

A number of workers have been examining some of the fundamental reactions which take place in the heated furnace and there has been some debate as to whether graphite plays a vital part in the formation of atoms. The other contributing factor influencing the 'chemical environment' of the heated furnace is the nature of the gas which envelopes it.

The type of inert gas appears to affect the nature of the graphite surface and also influences the species which are present within the furnace itself. For example, when nitrogen is used as inert gas, it is possible to form CN species in the heated tube which would not normally be possible if argon were chosen instead.

Absorption of oxygen onto active sites of the graphite can facilitate the formation of oxygen-containing molecular species of the analyte, and therefore influence the formation temperature of the analyte atoms. With the Varian CRA-90 configuration, hydrogen could be added to the inert gas in order to provide a more reducing environment. Hydrogen can improve the sensitivity of some elements with that design of furnace.

Some studies have been made with various metallic compounds (8, 9, 10) sometimes deposited on a graphite substrate. Other workers have examined metal atomizers (11-12) and have obtained some information about the role that carbon plays in the decomposition and atomization process.

Lanthanum or zirconium solutions have been applied to uncoated graphite tubes. Improved detection limits resulting for chromium, beryllium, manganese and aluminum were attributed to the lack of contact of the sample with the graphite (because carbides of the lanthanum or zirconium cover the graphite surface). Improved atomization efficiency via a thermal decomposition process was claimed (8).

Tantalum (in HF solution) has been allowed to soak into (non-pyrolytic coated) graphite tubes to form tantalum carbide on the graphite surface (9) when the tubes were subsequently programmed at 2500°C. In that study, substantially improved lifetimes of the graphite and stability of the signal were found for some elements.

A machined tungsten crucible, coated in situ with a carbide coating was found to be suitable for the analysis of copper in biological samples and yielded a longer useful lifetime than some pyrolytic coated tubes (10).

Atomization of samples from a pure tungsten tube furnace (designed to fit into a CRA-63 or CRA-90) has provided useful information on the reduction mechanism that occurs prior to atomization (11, 12).

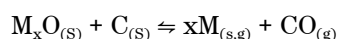
Atomization was successfully reported for silver, aluminum, barium, cadmium, cobalt, copper, magnesium, manganese, nickel, lead and vanadium, although characteristic concentration was somewhat worse than for pyrolytic coated graphite tubes. The short (5 mm) length of the metal furnace compared with the standard CRA-90 furnace could account for some of this loss of sensitivity.

The ability of these metal furnaces to easily atomize elements such as barium and vanadium (which require a high atomization temperature) suggests that the absence of carbon in the furnace may be an advantage.

Potential advantages claimed for metal atomizers include lower power requirements, and no problems with carbide formation. However, metallic atomizers can suffer from several important disadvantages:

- Their mechanical resistance may decrease after extensive heating.
- Inter-metallic compounds can form between the metal surface and the analyte, resulting in pronounced memory effects, severe loss in sensitivity, and sometimes both.
- Their chemical resistance is lower, leading to corrosion problems.

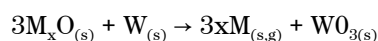
The appearance temperature of the analyte in various atomizers gives an indication whether or not analyte oxide reduction plays a role in the formation of analyte atoms. Lower appearance temperatures in graphite atomizers compared with metal atomizers are indicative of the following reduction process:



Comparisons have been made of the appearance temperatures for a number of elements from a tantalum strip and a graphite rod atomizer.

It was concluded that graphite probably acts as a reducing agent in the atomization of cobalt, iron, nickel and tin (14). In the same study, it was established that interferences may originate both on the surface of the graphite and in the vapor phase.

Whereas tungsten itself could act as a reducing agent by means of the reaction



tungsten trioxide will form a coherent stable film over the surface of the metal, effectively preventing any further reaction with the metal.

Sychra et al (11, 12) measured the appearance temperatures and atomization energies of aluminum, barium, cobalt, nickel, lead and vanadium, from a graphite tube (in argon) and a tungsten tube (in argon and argon/hydrogen).

Their results supported the following conclusions:

- Hydrogen facilitated the atomization of aluminum, barium and vanadium from the tungsten furnace.
- Thermal dissociation of the analyte species took place without intervention of reduction reactions of the analyte oxide with the metal of the tungsten atomizer.

In addition, lower appearance temperatures were found for aluminum and lead from a graphite furnace, suggesting some chemical reduction reaction with graphite.

It is clear, then, from the continuing studies on the mechanism of atom formation in graphite furnaces, that the heated carbon plays a significant role in the formation of analyte atoms, through its reducing properties. The nature of anions present, and the type of gas that surrounds and protects the heated graphite, also contribute to the reactions that take place in the furnace (for further reading on this subject see references 15 to 29).

Recent work has shown that the partial pressure of oxygen in a furnace appears to be much lower than previously thought. Sources of oxygen include traces from the inert gas and through thermal dissociation of oxides from the analyte (284). Such knowledge has led to means by which the partial pressure of free oxygen can be reduced and ascorbic acid, used as a chemical modifier, has achieved this goal (285).

However, debate continues on the subject of the partial pressure of oxygen in graphite furnaces and its effect on reactions in the furnace (286). Results of studies on reactions and on those factors which affect atomization have been reported (287, 288).

Most studies support the conclusion that a desirable configuration for graphite furnace AA would include the following design features:

- The atomizer should be tubular to improve the vapor-tube wall thermal equilibrium.
- The atomizer should be constructed of pyrolytic graphite or have a pyrolytic coating.
- It should be capable of achieving high rates of heating.
- The atomizer tube should be sufficiently long to maintain atoms in the measuring zone.
- The atomizer tube should be of minimum cross-sectional area to improve the peak sensitivity.
- Pyrolytic platform atomization should be available.

The design of the Varian graphite tube atomizers incorporates all these important features and has additional versatility in programming parameters to include protective gas type and gas flows.

Interferences

Many interference effects have been described in the literature and they can generally be categorized as being physical or chemical in the mechanism by which they are produced. Some rare spectral interferences are also found in atomic absorption analyses.

Physical effects of viscosity and surface tension are less important than with flame AA, but nevertheless they can affect the reproducibility of sample dispensing. The main effect is in the degree to which the sample spreads inside the graphite tube.

Attenuation of the incident hollow cathode radiation due to light scattering or to molecular absorption in the graphite tube can cause a false analytical signal unless it is corrected. Such absorption (or attenuation) is typically called background absorption or non-atomic absorption and is quite common in graphite furnace AA. For most practical analyses, it is essential to use background correction for graphite furnace work.

The Zeeman background correction technique is designed to correct for errors which would otherwise arise due to non-atomic absorption. The instrument will collect for non-atomic absorption which occurs during the analyte measurement period.

Spectral interferences are quite rare with Zeeman background correction although some examples have been quoted in the literature. Such interferences occur when the absorbing lines from a matrix element are situated close to the analyte emission line. When the magnetic field is on, the Zeeman shifted spectral components of the matrix element overlap the analyte line and give an error in the measurement. Recent detailed studies have found some examples including the effect of cobalt on gold (289, 290).

Chemical interference effects normally demand much more consideration in order to ensure that an accurate answer is obtained from an analysis. These effects could be categorized as follows:

Volatile compound formation, where the analyte element is lost at a relatively low temperature, perhaps during a dry or ashing stage, without undergoing atomization. For example, many metals form stable covalent chlorides and, in the presence of a large excess of the chloride ion, the metal may volatilize as the chloride compound before decomposition to the metal can take place (30). This is known to occur for elements such as lead, tin and zinc. Co-evaporation with large quantities of matrix metal chlorides, can result in severe loss of the analyte. This effect can be minimized by certain chemical modifiers discussed later.

Stable compound formation in which one or more relatively stable compounds of the analyte element are formed. More than one atomization peak could result because the appearance temperature will depend on the structure of the intermediate chemical form of the element (6, 31, and 32). In a similar context, some elements form stable carbides which do not readily decompose even at high atomization temperatures. Such carbide formation may reduce the analytical sensitivity of the element, and/or result in a significant memory signal, i.e. the signal obtained from a second atomization without further sample addition. Those metals which do form carbides but which can still be analyzed in graphite furnaces include barium, vanadium, molybdenum and titanium. However, there are metals such as tantalum, tungsten and zirconium which cannot be successfully analyzed largely because of stable carbide formation.

Controlled chemical interference effects (sometimes called matrix modification) can be used successfully in changing the appearance temperature and improving the sensitivity of the analyte, or changing the appearance temperature and magnitude of non-atomic absorption due to the matrix. Thus it is possible to separate, in time, the non-atomic absorption due to the matrix components and the analyte atomic absorption. This will lead to improved analytical accuracy.

Pyrolytic platforms are also used in furnace AA to minimize vapor phase interferences and to separate the atomic signals from the non-atomic signals. Use of the platform, together with chemical modification, can provide major benefits in practical analysis.

Chemical Modification of the Sample

It is worthwhile considering some definitions of atomization temperatures in attempting to learn about chemical interferences and reaction mechanisms which occur in graphite furnaces.

There are essentially two possibilities for the definition of atomization temperatures:

- The first appearance of the atomic absorption signal above the noise (defined as a signal equivalent to twice the standard deviation of the baseline), referred to as appearance temperature; and
- The temperature corresponding to the maximum of the atomic absorption peak, referred to as the peak atomization temperature.

Studies have shown that whereas the appearance temperature varied with analyte concentration (for Cu) the peak atomization temperature was independent of the analyte concentration (33).

Clearly the peak atomization temperature would be the only meaningful measurement when examining the effects of chemical modifiers.

It has been confirmed that the peak atomization temperatures for lead, cadmium and zinc (which were present as nitrates) increased in the presence of large excess of phosphoric acid:

Example:

Pb 800° → 9400 °C

Cd 470° → 620 °C

Zn 720° → 830 °C

It was proposed that pyrophosphates of these elements were formed. These compounds are stable up to about 900 °C and then decompose directly to the metal. This property of phosphoric acid has been used to reduce the volatility of lead and cadmium (6, 36), and produce single atomization peaks rather than a number of broad peaks.

It is desirable to chemically modify the sample in such a manner for certain relatively volatile elements in order to:

- Shift the atomization temperature to a higher (or lower) value, in order to prevent simultaneous appearance of atomic and non-atomic absorption. (Accuracy of analysis is likely to suffer if the atomic peak is coincident with a large non-atomic absorption peak.)
- Permit a higher 'ashing' temperature (by reducing the volatility of the analyte) and thereby enabling removal of non-atomic material prior to atomization.
- Improve the analytical sensitivity by ensuring that a single atomization peak appears rather than broad peaks which result from the decomposition and atomization of a number of different molecular species present in the sample.

Several chemical modifiers have been applied to the analysis of trace metals by graphite furnace AA. Table 1 summarizes those which have been used successfully and includes comments on the effects of the modifiers. Studies of this nature are continuing and it would be worthwhile reviewing the latest literature in the analytical chemistry field to learn of new techniques.

The modifier can be added to the sample inside the graphite tube and it is desirable to use a volume of modifier at least equal to that used for the sample. This means a more thorough mixing of the excess modifier with the sample will be ensured. Alternatively, the chemical modifier can be pre-mixed with the sample prior to the analysis. Some trial-and-error may be needed to establish whether it is better to pre-mix or add modifier to the sample in the furnace. If, for example, a precipitate is likely to form, the modifier should be added in the furnace. The furnace autosampler can be programmed to automatically dispense the required volume of modifier together with the sample into the graphite tube or platform.

The addition of NH_4NO_3 to a seawater sample has been effective in the measurement of copper. Not only was the background signal reduced, but the copper signal was substantially increased (39). This review paper gives examples of chemical modification in the analysis of other elements. See also reference 302.

More recently it has been found that a 2% solution of ammonium oxalate also acts in a similar manner to ammonium nitrate and may well be preferred. (293)

The ability of certain complexing agents to produce a stable complex which has a lower atomization temperature has been demonstrated in the case of lead (40).

Table 2 shows peak atomization temperatures for lead in 1% sodium chloride. Strong complexing agents for lead such as EDTA and citrate and oxalate ions reduce the atomization temperature. On the other hand, phosphoric acid increases the atomization temperature significantly when compared with a nitrate medium. This characteristic can be useful when it is necessary to shift an atomic peak away from coincident non-atomic absorption. Similar effects could also apply for other elements.

Studies on the effects of ascorbic acid on various elements have been carried out. Results showed that in the presence of ascorbic acid the peak appeared earlier for lead, and later for tin, manganese, molybdenum and vanadium (313). Interferences were also suppressed in some cases.

Recent work has shown that significant benefits can be obtained by using a palladium solution together with a reducing agent (368). The reducing agent (such as ascorbic acid or hydroxylamine solution) was added to reduce palladium to a lower oxidation state from which the greatest benefit was obtained. Such a combination of modifiers stabilized the signal for a number of analytes and permitted the use of higher ashing temperatures (see also Chapter Four and Chapter Eight).

Table 3 shows modifiers and other chemical agents which have been used to assist in the determination of a variety of sample types. Of these listed chemicals, only the Triton X-100 solution acts to assist in sample handling. The other chemicals listed assist in the removal of the matrix background and enhance the atomic signal discrimination.

Further details on the analytical treatment of individual sample types will be found in Chapter Seven.

In general whenever an analyte presents a problem due to its high volatility, where an analyte and matrix volatilize at similar temperatures, a study of a chemical textbook or handbook is recommended to determine whether there are any compounds of the analyte which have high melting or decomposition temperatures.

Knowledge of the decomposition temperature and the intermediate compounds which could form during the decomposition, could also assist the choice. If such a compound exists, then the addition to the sample in the atomizer of the appropriate element or anion to form the compound either in solution or during the ashing step could well alleviate the problem.

Many of the chemical modifiers listed in Tables 1 and 3 have been chosen by such means.

Table 1. Chemical Modifiers for Specific Elements in Graphite Furnace AA

| Analyte | Modifier | Effect | References |
|---------|---|--|-----------------------|
| Ag | NH ₄ H ₂ P ₀ ₄ (1% solution) | Permits a higher ashing temperature. | 293, 306 |
| As | Ni (50 µg/mL) | Permits a higher ashing temperature and enhances the signal. | 34,37 |
| | Pd or Pt (100 µg/mL to 2 mg/mL) | Permits a higher ashing temperature and enhances the signal. | 291, 292 |
| Au | Ni(NO ₃) ₂ (0.25% solution) | Permits a higher ashing temperature. | 306 |
| B | Ba(OH) ₂ (100 µg/mL) or La(NO ₃) ₃ (1000 µg/mL) | Signal enhancement | 35 |
| Bi | Pd or Ni (1000 µg/mL) | Permits a higher ashing temperature and enhances the signal. | 293 |
| Cd | H ₃ P ₀ ₄ or NH ₄ H ₂ P ₀ ₄ (1000 µg/mL) | Conversion to less volatile phosphate which atomizes at a higher temperature. | 36 |
| Ga | Ni(NO ₃) ₂ (1 mg/mL) or Pd (0.05% solution) | Permits a higher ashing temperature and enhances the signal. | 294 293 |
| | Pd (0.05% solution) | Permits a higher ashing temperature and enhances the signal. | 293 |
| Hg | Pd (0.1% solution) | Permits a higher ashing temperature and enhances the signal. | 295, 293 |
| | (NH ₄) ₂ S in excess. | Stabilizes the signal | 38 |
| In | Pd (0.1% solution) | Permits a higher ashing temperature. | 296, 293 |
| P | La or Ni (0.2% as nitrate) | Permits a higher ashing temperature and improves precision. | 41 |
| Pb | H ₃ P ₀ ₄ or NH ₄ H ₂ P ₀ ₄ (5000 µg/mL) | Permits a higher ashing temperature and stabilizes the signal. | 6, 33, 36 297, 298 |
| | EDTA, citrate, oxalate (0.5% - 1% v/v) | Stabilizes lead which atomizes at a lower temperature than does a nitrate or chloride matrix | 40 |
| Sb | Ni(NO ₃) ₂ (50 µg/mL to 1000 µg/mL) | Permits a higher ashing temperature and stabilizes the signal. | 34,37 |
| | Pd (NO ₃) ₂ (100 µg/mL with ascorbic acid (2.5%). | | 299,293 |
| Se | Ni(NO ₃) ₂ (50 µg/mL) | Permits a higher ashing temperature and enhances the signal. | 34, 37, 300 |
| Sn | Diammonium hydrogen citrate (0.1% solution) | Complexes with tin and enhances sensitivity. | 40 |
| | Pd (500 µg/mL) | Permits a higher ashing temperature and enhances the signal. | 293 |
| Te | Ni(NO ₃) ₂ (0.1% solution) | Permits a higher ashing temperature and enhances the signal. | 306 |
| Ti | H ₂ SO ₄ (1% solution) | Stabilizes the signal. | 293, 307, 308 |

Table 2. Chemical Modification of Lead in 1% Sodium Chloride*

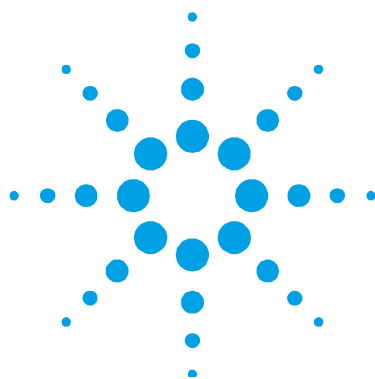
| Modifier | Peak Atomization Temperature °C for Lead |
|------------------------------------|--|
| 0.5% EDTA | 560 |
| 1% NH ₄ Citrate | 610 |
| 1% NH ₄ Oxalate | 700 |
| 1% NH ₄ Acetate | 870 |
| 1% NaCl | 910 |
| 1% HNO ₃ | 970 |
| 1% NH ₄ NO ₃ | 980 |
| 5% H ₃ PO ₄ | 1180 |

*Background Peak (1% NaCl) 1080 °C

Half peak range 880 °C – 1150 °C

Table 3. Chemical Modifiers for Specific Matrices in Graphite Furnace AA

| Interfering Species | Analyte | Modifier | Effect | References |
|--|---------------|--|---|-----------------|
| NaCl | Cu, Pb, Cd | NH ₄ NO ₃ or NH ₄ oxalate (2% solution) | Removal of NaCl through formation of NH ₄ Cl (reduction in non-atomic absorption). | 37,42 51, 52 |
| NaClO ₄ Alkali metal halides; Al, Mg halides. | Cu | Na ₂ O ₂ (3000 µg/mL) | Substantially reduced interferences caused by these salts in water and seawater. | 43 |
| Seawater | Cr, Ni | Mg(NO ₃) ₂ or HNO ₃ (1% solution) | Reduces background signal, minimizes interferences. | 293, 310 |
| | Mo, Mn, Pb, V | Ascorbic acid (10% sol'n.) | Suppresses matrix interferences. | 309 |
| Blood | Pb | 0.1% Triton X-100 | Dispersing Agent — facilitates dispensing. | 311 |
| Serum and Blood | Al, Cr, Mn | Dilute Triton X-100 | | 312, 311 |



2. The Zeeman Effect in Furnace AA

Ideally, during the measurement period in furnace AA, the only absorbing species within the optical beam should be the analyte atoms. In practice, however, other species may be produced during the sample atomization process. If these species are capable of absorption at the analyte wavelength, and this absorption overlaps in time the atomic absorption of the analyte, the resulting absorbance measurements will be higher than they should be for a given atom population and the analytical result will not be valid (314, 315). As discussed in Chapter Three, the two main sources of this background absorption arise from the scattering of the resonance radiation by solid particulate matter and the absorption by molecular species formed during the sample matrix decomposition.

In the first instance, the furnace temperature program should be optimized or the technique of matrix modification exploited with a view to separating in time the analyte absorbance from the background absorbance. These techniques are discussed in Chapters One and Three. Often, such a complete temporal separation of the analyte and background signals is not possible and it then becomes essential to employ a spectrophotometric system capable of correcting for this systematic error.

The perfect background correction system would provide a means for measuring the total absorbance of the analyte in combination with the background, and simultaneously provide a reference measurement due to all of the absorbing species except the analyte. Acceptable correction for background absorption can be achieved when these measurements are made sequentially providing that their separation in time is small compared to the rate at which the absorbance signal is changing.

Historically, the initial attempt to provide this reference measurement was achieved by incorporating a deuterium continuum source into the spectrometer's optical system (316). This technique relies on three assumptions:

- Scattering by particulate matter is constant over the bandwidth typically used (0.5 nm).
- The molecular absorption of matrix components is also constant over the bandwidth
- The atomic absorption line is much narrower than the bandwidth (0.002 nm vs 0.5 nm).

Within these assumptions, the absorbance measured with the hollow cathode lamp includes the contributions from the analyte, matrix and scattering components while with the deuterium lamp there is essentially no residual atomic absorption. Measurements of absorbance from both sources are subtracted to provide a background corrected atomic absorbance. While this technique is often adequate in many analytical applications, it will clearly fail should the matrix components present discrete line spectra. Furthermore, no simple, single tunable source is capable of adequately covering the entire ultra violet – visible range required for atomic absorption and whenever multiple sources are employed, careful optical alignment is imperative to ensure identical spatial distribution of source radiation within the furnace.

Background correction approaches using two separate line sources have also been suggested for use in atomic absorption (317). However, such an approach is not generally applicable and suffers more or less from the same limitations of the continuum lamp technique.

Modern physics has shown that the wavelength of atomic spectral lines can be shifted by a variety of techniques. The application of magnetic fields (Zeeman Effect) and electric fields (Stark Effect) have been widely exploited, although a number of other more sophisticated approaches are also known (318, 319). The Zeeman Effect has proved the most practicable and Varian pioneered the application of this technology to atomic absorption.

By employing the Zeeman Effect to modify the atomic absorption wavelength profile, the residual background absorbance at the analyte wavelength, can then be measured separately. Since only a single source is required, there remain none of the optical alignment problems encountered with multiple source schemes with their associated loss of accuracy. Furthermore, the Zeeman Effect is generally applicable to all spectroscopic transitions and so encompasses the entire wavelength range. The application of the Zeeman Effect in atomic absorption goes a long way towards providing the ideal correction for non atomic absorbance.

Theory of the Zeeman Effect

Despite the absence of a comprehensive atomic theory, the early spectroscopists were vigilant experimentalists who recognized the similarities between the spectra of many elements. We now understand these similarities in terms of their identical valence electronic configurations, the electrons that are usually involved in optical transition and the formation of chemical bonds.

The Dutch physicist Zeeman was no exception, since in 1897 he reported that atomic spectral lines were observed to split into a number of components under the influence of a strong magnetic field (320). Furthermore, many atomic lines spanning a variety of elements, exhibited identical splitting patterns in such a magnetic field. That is, for a magnetic field of given intensity and orientation, many lines split into just three components with the same spacing (Figure 9). The center line remained at the original wavelength while the other two multiplet components were symmetrically displaced about this central component. It was further observed that spectroscopic transitions, in either emission or absorption, involving the central, or pi (π) component, always involved optical radiation polarized parallel to the direction of the applied magnetic field. Likewise, spectroscopic transitions involving the other two, or sigma (σ), components always involved radiation polarized perpendicular to the magnetic field. This purely empirical behavior of many spectral lines was referred to as the Normal Zeeman Effect.

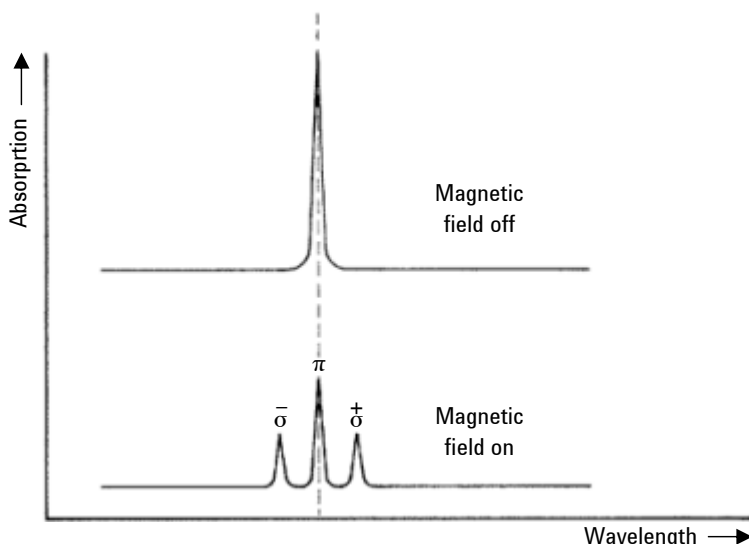


Figure 9. Example of the normal Zeeman effect (Cd at 228.8 nm)

Subsequently, more comprehensive observation of the Zeeman Effect revealed the existence of far more complex splitting patterns than the simple Normal Zeeman Effect. In these cases, the original line became split into a variety of lines, usually more than three (318, 319, and 321). These splitting patterns were field strength and orientation dependent and once again the individual multiplet components could be distinguished by their polarization characteristics. This more complex behavior of atomic spectral lines became known as the Anomalous Zeeman Effect. In general such splitting patterns for typical field strengths are characterized by a number of π components closely centered about the field free wavelength and multiple σ components both to higher and lower wavelengths (see Figure 10 for typical examples).

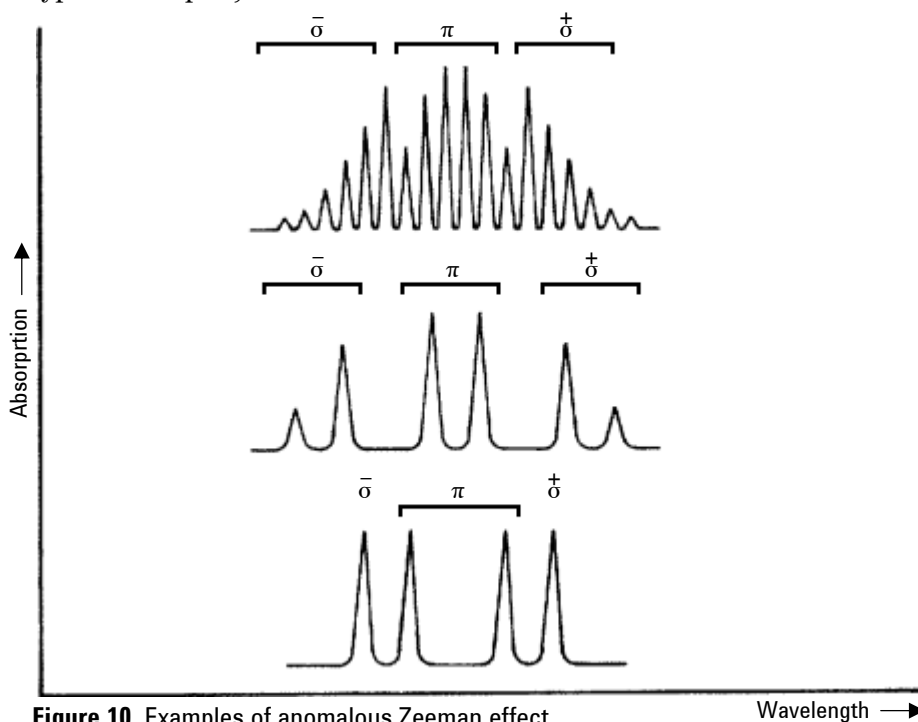


Figure 10. Examples of anomalous Zeeman effect

Though of little consequence to the practical aspects of understanding the application of the Zeeman Effect to atomic absorption, the advent of modern quantum theory now provides an explanation for these observed characteristics of the Zeeman Effect. In terms of this theoretical framework, atomic absorption spectral transitions are explained as resulting from the interaction of the source radiation with the outer valence electrons as they move about the atomic nucleus.

These motions are further described in terms of the angular momenta of these electrons due to their orbital motion in combination with a spinning motion, though caution is required in using such mechanical analogues.

Quantum theory tells us that the energy of these electrons is determined by the mutual coupling of these sources of angular momentum. Recalling the vector nature of angular momentum, when an atom is subjected to an applied magnetic field, the electron's energy is further dependent on the orientation of its total angular momentum with respect to the applied field direction. Described simply, the observed Zeeman splitting patterns are the result of the small but observable energies associated with the possible changes in this relative orientation.

The magnitude of these energies is directly proportional to the intensity of the applied magnetic field. When only electronic orbital angular momentum is involved in a given spectroscopic transition, the Normal Zeeman Effect is observed, but in the more general case, involving in addition, electron spin, we encounter the Anomalous Zeeman Effect. The classification of the various multiplet components into either π or σ polarization can also be explained on the basis of quantum theory but a discussion of this aspect is beyond the scope of this brief introduction to the Zeeman Effect (318, 319).

Experimental Zeeman Atomic Absorption

Several experimental arrangements are possible when exploiting the use of the Zeeman Effect in atomic absorption. Firstly, the field can be applied to either the lamp or to the sample since the Zeeman Effect applies both to absorbing and emitting species. Standard hollow cathode lamps do not operate satisfactorily in the strong magnetic fields required. Even if acceptable operation were achievable, the split lamp emission profile would result in the background absorption being measured at wavelengths slightly removed from the analyte absorption wavelength. Consequently, if the background contained discrete spectral features, this approach could lead to inaccurate background correction. By applying the field directly to the absorbing sample, standard hollow cathode lamps can be used and the background absorbance is measured at the same wavelength as that of the analyte and so correction for structured background features is optimized.

Accepting the preference for applying the magnetic field to the absorbing sample, it is possible to use either a fixed or modulated field. With a magnetic field fixed in time, the sample and background measurements are discerned on the basis of their polarization characteristics by using a modulated polarizer. Such an approach does not achieve optimum sensitivity for those atomic transitions exhibiting the Anomalous Zeeman effect, and experimental problems associated with the modulation of the polarizer lead to a degradation in the background correction accuracy.

With a modulated magnetic field, a fixed polarizer is included and oriented so as to reject the component of the hollow cathode lamp emission polarized parallel to the magnetic field. With the field off, the total absorbance of sample plus background is measured whereas when the field is on, the perpendicularly polarized light transmitted by the optical system can only be absorbed by the σ components and, in the ideal case, these are sufficiently shifted from the lamp resonance wavelength to result in zero atomic absorbance. However, the background species, being insensitive to the presence of the magnetic field, continue to absorb providing the background absorbance. The field off and field on absorbances are subtracted to yield the background corrected atomic absorbance. Furthermore, in taking this difference of absorbances, the absolute magnitude of the hollow cathode lamp intensity is cancelled out and so the Zeeman approach to atomic absorption provides, in a single beam optical system, the attributes of a double beam system. That is, changes in the source intensity that are slow relative to the rate at which the field is modulated are automatically compensated. Furthermore, since the π component of the absorbing transition is not used, no loss in sensitivity is encountered with the Anomalous Zeeman Effect.

This arrangement results in the best combination of analytical sensitivity and background correction accuracy. Figure 11 shows a schematic representation of the SpectrAA-30/40 Zeeman configuration.

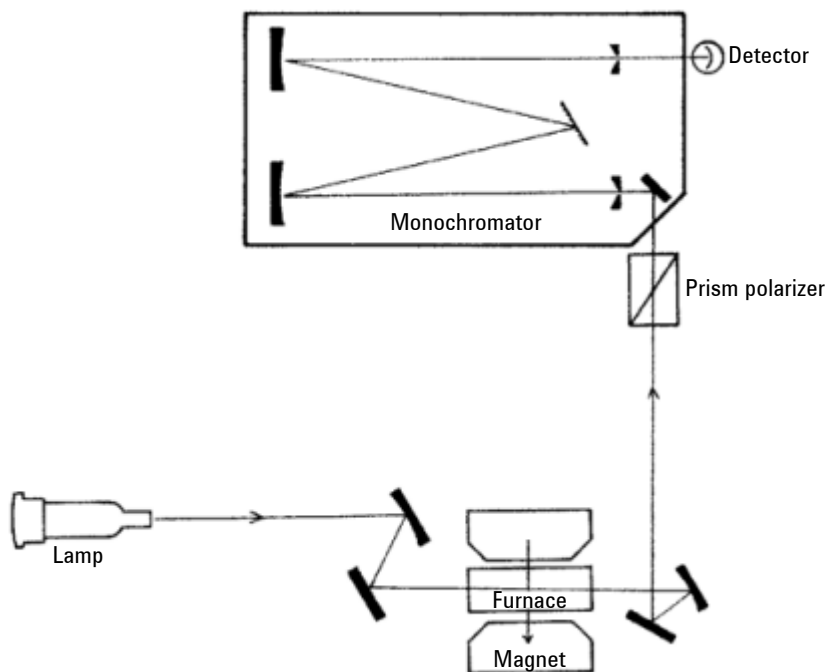


Figure 11. Optical configuration of Varian SpectrAA-40 Zeeman

Analytical Characteristics of Zeeman Atomic Absorption

As discussed above, with the magnetic field energized, the atomic absorbance is ideally zero and only the background absorbance is measured. However, in practice there may be some small residual atomic absorption due to:

- a The incomplete removal of the component of the hollow cathode lamp emission polarized parallel to the magnetic field.
- b Insufficiently intense magnetic fields being used such that the components are not adequately shifted.
- c The complex interaction of the hyperfine (ie. isotopic) structure of a given spectral transition.

In the SpectrAA-30/40 Zeeman a high quality crystal polarizer has been used so the rejection of the π component is, to all practical purposes, complete. In addition, the magnetic field intensity is high enough to minimize the effects of problems (b) and (c). Nevertheless, there is often an unavoidable but slight loss in sensitivity and the ratio of the Zeeman sensitivity to that of normal atomic absorption is defined as the magnetic sensitivity ratio (MSR). MSR values for the most common atomic absorption lines are listed in Chapter Four and it will be apparent that for the majority of elements the loss in sensitivity with the Zeeman system is minimal and is more than compensated for by the superior background correction accuracy.

Calibration curves in conventional atomic absorption, generally asymptote towards a limiting absorbance at high concentrations (Figure 12). This is due to differences in the emission and absorption profiles, the presence of nearby non absorbable spectral lines passed by the monochromator, and residual stray light within the spectrometer's optical system. In Zeeman atomic absorption, there is the further complication that when the field is applied, there may still be some small residual atomic absorption which can result in the analytical curve bending over at high concentrations (322). This phenomenon of reflex curvature means that two different concentrations can give the same absorbance, a clearly unacceptable situation. The SpectrAA-30/40 Zeeman system constantly monitors the peak absorbance value during the atomization process and indicates an error when the maximum permissible absorbance, slightly below the reflex point, is exceeded. Conceptually, the reflex curvature phenomenon in Zeeman atomic absorption can be understood by viewing the Zeeman corrected absorbance as the result of subtracting the Zeeman background absorbance from the total Zeeman absorbance. As a function of concentration, the total absorbance measurement asymptotes to a limiting value at a greater rate than does the background measurement and the net result of subtracting these two curves results in a reflexing of the analytical curve.

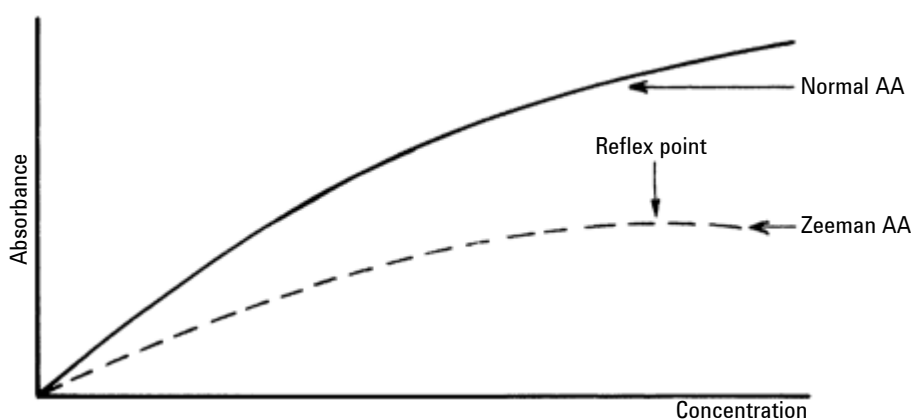
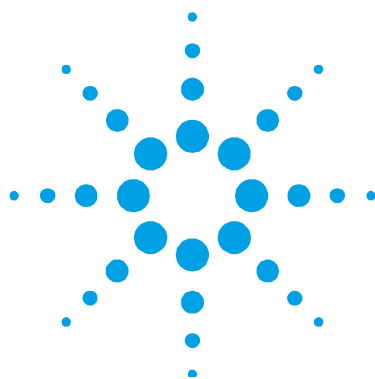


Figure 12. Calibration curve for normal and Zeeman atomic absorption

In choosing the analytical wavelength in atomic absorption, the major considerations are the measured sensitivity and the analytical working range. However, using Zeeman atomic absorption there are the additional complications of MSR and reflex curvature. Different lines of a given element may exhibit significantly different values of MSR or degrees of calibration curvature and these must be also considered in choosing the optimum analytical wavelength. In some cases, the selected wavelength will be different from that preferred for conventional atomic absorption. In Zeeman AA, for example, the 327.4 nm wavelength for copper yields comparable sensitivity and more linear calibration curves compared with the 324.7 nm wavelength preferred for non-Zeeman AA.

Finally, the measurements of the total and background absorbances are made sequentially, thereby admitting the possibility of dynamic measurement errors associated with rapidly changing absorbance levels. To minimize these effects the magnetic field is modulated at twice the mains frequency (100 or 120 Hz) and furthermore the SpectrAA-30/40 Zeeman software incorporates a polynomial interpolation routine such that the two absorbance measurements are effectively made at the same point in time (323).

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3. Development of Analytical Programs

General

The graphite tube atomizer system has facilities for the programming of a number of parameters including temperature, time, gas flow rate and type. In addition, memory facilities for the storage of programs are a feature of the instrument. A complete description of the atomizer controls and instructions for programming the atomizer are contained in the Operation Manual. The DS-15 unit incorporates a CRT display, which is used to display the parameters selected for the operation of the furnace as well as giving a graphical presentation of the variation of absorbance with time during any selected portion of the temperature cycle.

The recommended conditions (wavelength, lamp current, spectral band pass, Maximum absorbance) are given in Chapter Four; specific methods are given in Chapter Seven.

The installation of the atomizer and alignment in the light path are described in the Operation Manual and are not repeated here. The most important point to note in the alignment of the atomizer is that the position of the atomizer must be adjusted to give the maximum intensity of transmitted light from the hollow cathode lamp.

Selection of Operating Parameters

The objective is to select operating parameters which will completely desolvate the sample, remove the maximum amount of matrix material during the ash stage, provide adequate analytical sensitivity and separate the analyte peak from non-atomic absorption peaks.

Selection of Temperature and Time Parameters

Dry Stage

The desolvation (or dry) stage of the program plays an important role in determining analytical precision.

The temperature and time are chosen to give complete desolvation of the sample before the ash stage is reached. The desolvation temperature and time for a particular sample will depend on the nature of the solvent and the sample volume. Generally, the temperature is set just below the boiling point of the solvent to ensure a sufficiently high rate of vaporization of the solvent. If the temperature is too high the sample may spatter, resulting in the loss of sample to the extremities of the furnace tube or on to the end windows of the atomizer. The same effect may occur if the time is not sufficiently long and the temperature ramp to the ash stage commences before desolvation is completed.

The temperature program for desolvation of samples containing two or more solvent constituents, such as strong aqueous acid solutions or mixed organic solvents, may be adjusted to take account of the different boiling points of the solvents. The first temperature of the desolvation stage is programmed in relation to the lowest boiling constituent of the solvent. As the most volatile solvent is removed, the temperature may be increased to effect vaporization of the less volatile solvent.

For example, a sample in 5% aqueous nitric acid may be programmed initially for desolvation near the boiling point of water. As the vaporization proceeds, the solution will become more concentrated in nitric acid until the azeotropic mixture (b.p. 121°) is attained. The temperature is gradually increased to effect sufficiently fast removal of the remaining solvent.

It should also be noted that analytical precision may be influenced by any tendency for the sample droplet to spread over or run along the tube as the solvent evaporates. Such effects will be worse for organic solutions than for aqueous ones. Spreading or running of the sample droplet may be affected by the dry temperature and such effects will generally worsen with increasing temperature. The temperature for drying should be low enough to prevent the sample spreading past the central profiled section of the tube. Spreading will not usually present a problem with partitioned tubes because the sample is confined to the center of the tube. The dry temperature will be the highest temperature consistent with rapid vaporization of the solvent and the minimization of spreading or running effects.

The total dry time will usually be between one and three seconds per microliter of sample volume. For example, use 40 seconds dry time for a 20 μL volume of aqueous solution. For the same volume of organic solvent it may be possible to use a shorter time. For best precision, use sample volumes between 2 and 40 μL .

The pyrolytic platform will require the use of somewhat higher dry temperatures than those needed for sampling from the tube wall because the platform does not reach as high a temperature as the wall. See references 301 and 303 for further information about the selection of dry parameters when platforms are used.

In addition to the desolvation stage, an ash or char stage is usually necessary to further remove sample matrix components prior to the atomization stage. Matrix components may vaporize or decompose on heating to give background absorption resulting from absorption by molecular species or light scattering from particulate matter so that it is necessary to minimize the amount of matrix left in the tube when atomization begins. By ashing away the matrix, chemical interferences can also be reduced. With some samples, there may be little or no ashing required prior to atomization while other samples with complex matrices will require careful selection of the temperature and time parameters for ashing. These parameters are optimized for maximum removal of the sample matrix consistent with minimum loss of the analyte element. The ash temperature for organic matrices usually lies in the range 400 °C - 800 °C and the time is often comparable to the desolvation time. As with the desolvation stage, the atomizer may be programmed for ashing at several temperatures, depending on the complexity of the sample.

The recommended procedure to select the optimum ash temperature is to vary the ash temperature and measure the absorbance signal during the atomization stage. The maximum temperature for ashing is determined by increasing the ash temperature and measuring the background-corrected absorbance for the analyte. When loss of the analyte occurs during the ash stage, an observable decrease in the atomic absorbance will occur. Since the aim of ashing is to minimize the background as well, this process of increasing the ash temperature and observing the effect on the atomic signal should be carried out in parallel with measurements of the background absorbance; the background absorbance usually decreases with increasing ash temperature.

If there is too much background to permit accurate correction, then chemical modification of the sample should be attempted.

A guide to the maximum ash temperatures is given in Chapter Four. With a number of elements, the lowest temperature at which atomization commences depends on the composition of the matrix and each matrix should be checked for pre-atomization losses of analyte by the method described above. The ashing time depends in part on the amount of matrix and is usually from 10 to 30 seconds.

Once the temperature program for the ash step has been established, the background absorbance during subsequent steps should be checked to ensure that there is no detectable background at the start of the 'read' period. It is important that the light beam is not attenuated in any way at this time because the photomultiplier tube voltage is fixed at this instant. When a short step of 1 or 2 seconds duration with gas flow stopped is inserted before the atomize ramp step, the analyst can use the background only signal during this step to decide whether the ash time (with full gas flow) needs to be increased.

In many analytical situations, the analyte and background peaks can be separated more effectively by chemical modification of the sample (see Chapter One). Examples of chemical modifiers which change the volatilization of the analyte are given in Chapters One and Seven. With certain analyses, substantial background absorption occurs after the analyte absorption peak; the matrix can be chemically modified to reduce the atomization temperature of the analyte and give greater separation of atomic and background absorption peaks. An example is the determination of cadmium in sea water, where EDTA may be used to reduce the atomization temperature of cadmium (44).

For the same reason mentioned in the previous section, the ash temperatures needed when the pyrolytic platform is used will be higher than for wall ashing, generally by 100 °C. See references 301 and 303 for further information.

Specific examples of the optimization of the parameters for sample ashing are given in the introduction to Chapter Seven.

Atomization Stage and Heating Rate

The atomization temperature and the rate of heating of the atomizer from ash to atomize temperature (the ramp rate) affect the sensitivity of the analysis. Atomization temperatures vary from element to element and the optimum atomization temperature for a particular element may vary slightly according to the matrix. The figures given in Chapter Four as the atomization temperature for each element should be used in the first instance.

The variation of peak absorbance with atomization temperature for elements of high, medium and low volatility (cadmium, copper and vanadium) is shown in Figure 13.

Generally, the optimum temperature for elements in aqueous or mineral acid matrices will be the lowest temperature giving the maximum absorbance, since the lifetime of the graphite tube is prolonged at lower temperatures. These optimum temperatures are approximately 1300 °C for cadmium, 2100 °C for copper and 2700 °C for vanadium, as Figure 13 indicates.

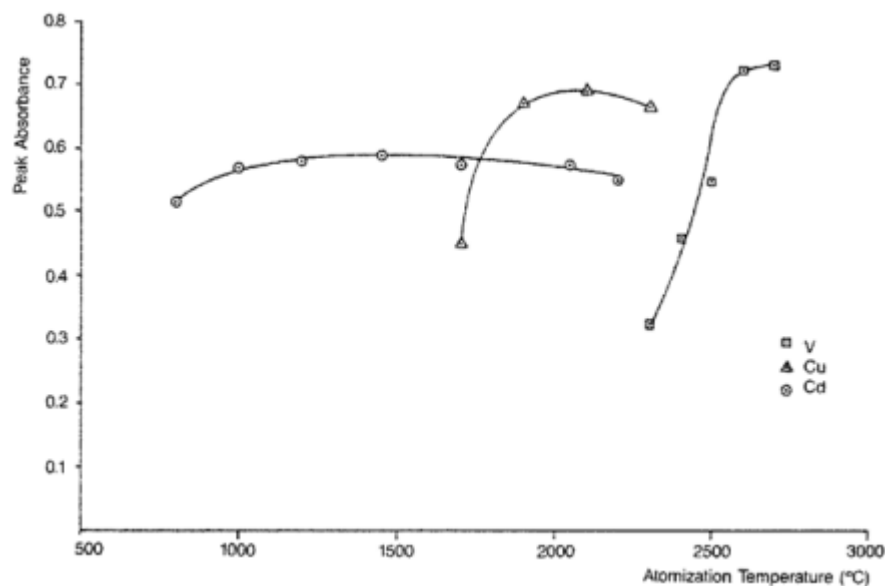


Figure 13. Effect of atomization temperature on peak absorbance

The peak absorbance does not show a continuous increase with atomization temperature because the rate of loss of atomic vapor from the atomizer also increases with temperature. Loss of atomic vapor occurs by diffusion, convection and expansion of the gas in the atomizer. The diffusion coefficient for removal of the atomic vapor increases with temperature according to the relationship:

$$D \propto T^m$$

where the exponent m varies between 1.5 and 2 (45), while expansion of the atomic vapor also increases with temperature. In consequence, there is a temperature at which the increase in the rate of analyte atomization with temperature is maximized with respect to the increase in the rate of loss of atoms from the light path.

In many analyses, however, and particularly those in which the sample matrix is relatively non-volatile, a higher atomization temperature may be necessary to ensure that matrix products do not accumulate in the atomizer. For example, an atomization temperature of 1300 °C for Cd would be too low for a seawater matrix and a temperature of 2000 °C or more would be necessary.

The atomization time is usually set as the minimum time required for complete vaporization and removal of the analyte and matrix from the atomizer. This is the time required for the atomic absorption signal to return to the baseline; when the graphite tube atomizer is programmed to display the atomization stage, this time is readily measured from the CRT display. It should be noted that this time interval can be decreased by increasing the gas flow rate (see 'Selection of Gas Flow and Read Parameters' later in this chapter).

With some elements of low volatility, such as strontium, vanadium, titanium and molybdenum, both the atomization temperature and time are important parameters in ensuring the minimization of memory effects. If the analyte element is not completely vaporized and removed during the atomize stage, an enhancement in the signal during the next atomization may result. The element may accumulate gradually in the atomizer, causing a gradual rise in absorbance over a series of atomizations. This effect is shown for strontium in Figure 14.

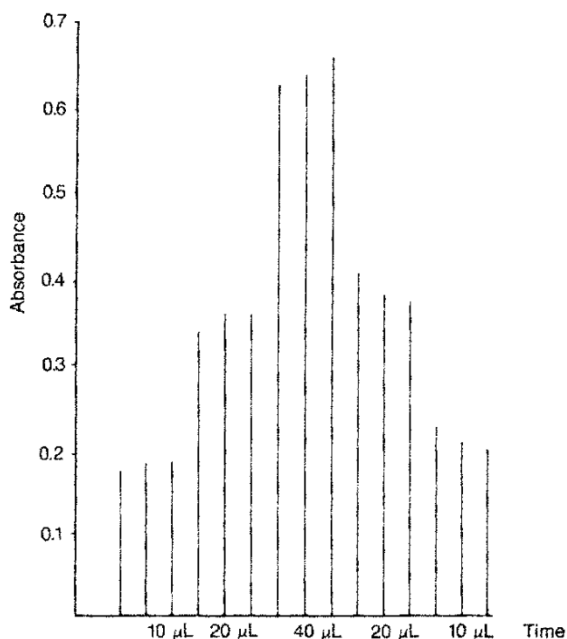


Figure 14. Memory effect for strontium

Atomization with the specified volumes resulted in an increasing peak absorbance with each volume. Problems of memory are overcome by increasing either the atomization temperature or the time, or both.

Memory effects may also be detected by carrying out blank firings of the atomizer (i.e. with no sample present). If the atomic signal for the blank firing following atomization is higher than the signal for subsequent blank firings, steps must be taken to minimize the memory effect.

The peak absorbance also depends on the ramp rate. The effect of ramp rate on peak absorbance for cadmium, copper and vanadium is shown in Figure 15.

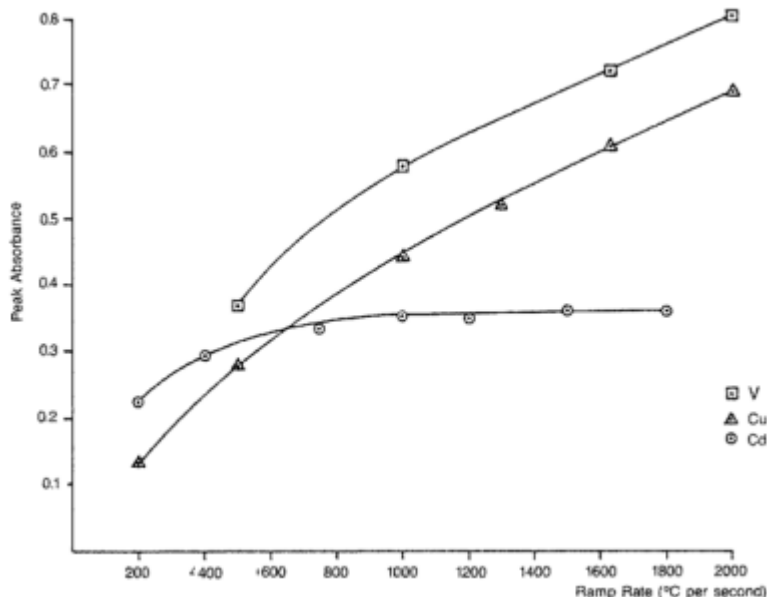


Figure 15. Effect of atomization ramp on peak absorbance

With cadmium, the peak absorbance reaches a plateau at a ramp rate of approximately 1000 °C per second while copper and vanadium show the greatest sensitivity at the maximum ramp rate (2000 °C per second). Generally, the less volatile the element, the more significant is the improvement in sensitivity with maximum ramp rate.

Modern atomic absorption spectrometers allow absorbance measurements to be made in either the peak height or peak area mode. For some applications, the choice will be straightforward; for others, it will be necessary to obtain experimental measurements to decide which method is best suited to the particular analysis.

Peak area measurements, for example, will often extend the calibration linearity. As shown in Figure 16, the calibration from peak area is clearly linear while the peak height calibration shows some curvature.

For many elements, the sensitivity of peak height measurement will be better than that of peak area measurement. This is especially the case with more volatile elements such as cadmium and lead which produce narrow absorbance peaks. With elements requiring high atomization temperatures, the peaks are broader and the peak area sensitivity may be comparable to peak height sensitivity.

The relative precision offered by the two methods of peak measurement will also vary according to analytical circumstances. Generally, it is preferable to use the method which gives the best compromise in respect of sensitivity, accuracy, linearity and precision.

With some analyses, the highest ramp rate is not always necessary. For example, when the atomic peak overlaps background absorption, an increase in the ramp rate will result in less separation of the atomic and background peaks; this will affect the accuracy and precision of background-corrected absorption measurements.

When platforms are used, the maximum ramp rate for atomization should be used. Also, it is desirable to use as high an atomization temperature as is practicable, for two reasons. First, the atomic signals become sharper with increasing temperature and, secondly, the chemical interferences are often reduced at higher temperatures. The atomization temperature should be as high as possible consistent with the atomic signal occurring within the constant temperature portion of the atomization temperature profile.

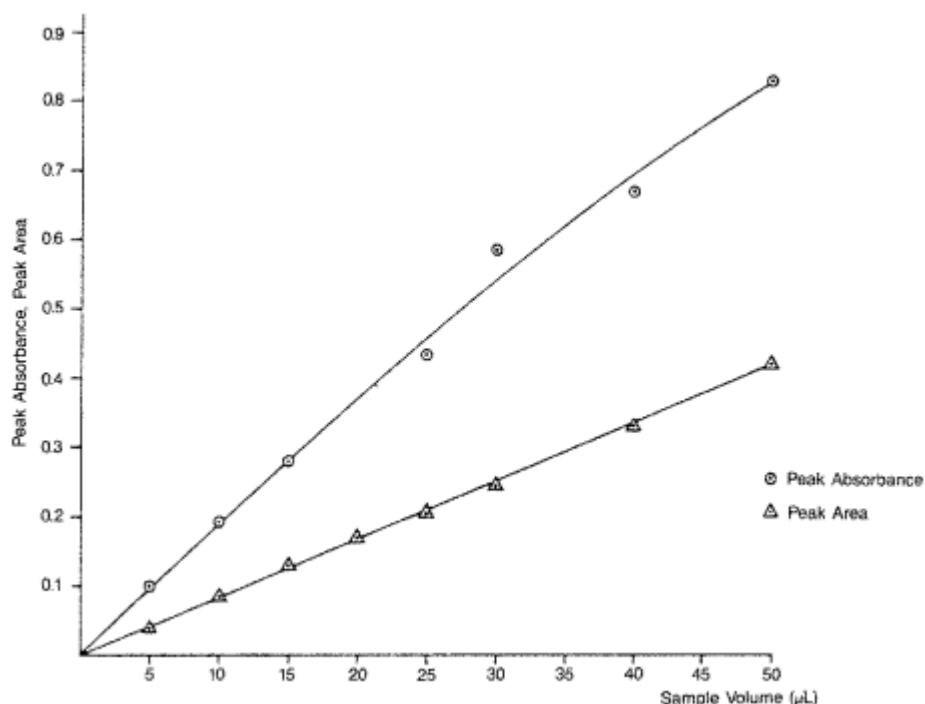


Figure 16. Peak absorbance and peak area calibration graphs for copper

Selection of Gas Flow and Read Parameters

A flow of inert gas through and around the graphite tube serves to remove the sample components from the atomizer at each stage of the analysis and to protect the graphite tube from oxidation. The preferred inert gas is argon but nitrogen can also be used.

During the dry and ash steps of the analysis, the total gas flow through the atomizer should be programmed for the maximum rate of 3.0 L/min, since the most efficient removal of the products of these steps will occur with the highest flow rate.

During the atomization stage, the gas flow may be reduced to zero thus improving sensitivity for the analyte element; this effect is a result of the increase in residence time of the atomic vapor within the optical path. Generally, the best sensitivities will be realized when the gas flow rate during the atomization stage is programmed at zero.

Figure 17 shows the variation in absorbance with gas flow rate during atomize for several elements.

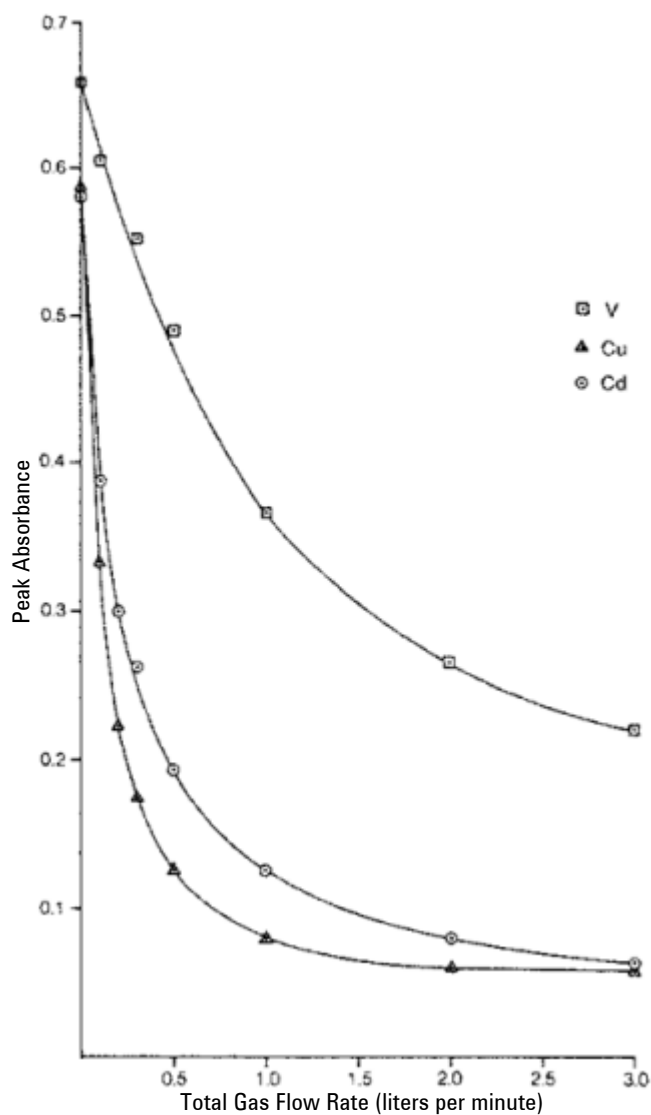


Figure 17. Variation of peak absorbance with inert gas flow rate during atomization

It should be realized that interruption of the gas flow during the atomization stage will shorten graphite tube lifetimes, due to increased exposure of the hot tube to atmospheric oxygen. Therefore, it is desirable that the gas flow be reduced or stopped for as short a time as possible during the atomize stage. The time for which the gas flow is reduced should be programmed for each element and matrix in relation to the minimum time required for collection of the necessary information on the analyte peak absorbance, area etc. With elements requiring high atomization temperatures, the absorbance peak may be quite broad and the tail of the peak may extend for several seconds after the maximum. When the gas flow is stopped, resumption of the flow shortly after the peak maximum will minimize degradation of the graphite tube. With this procedure, the choice of measurement method will depend on the relative precision of the two methods and the relationship between response and concentration.

For the same reason, it is desirable that the inert gas used during the high temperature stages of the cycle be of as high a purity as possible.

Atomization in an argon atmosphere will give better sensitivities than those obtained in a nitrogen atmosphere and graphite tube lifetime is usually considerably longer when argon is used.

For some elements, such as barium and europium, the improvement in sensitivity with the use of argon is several-fold and is related to differing chemical processes occurring in the furnace with the two gases. For most other elements, the improvement with argon is slight and results from the slightly lower diffusion coefficient of atomic vapor into argon, since the diffusion coefficient is inversely proportional to the square root of the molecular mass.

The gas type ('normal' or 'alternate') may be programmed on the graphite tube atomizer for any stage of the program. This facility may be used in a number of ways. A low purity sheath gas may be used during the pre-atomization stages of the cycle and a higher purity gas during the atomization stage. With elements that show a marked difference in sensitivity between nitrogen and argon, the use of argon may be reserved for the atomization stage. Furthermore, a reactive gas such as oxygen may be used during the ash stage. It has been shown that for certain analyses, the use of oxygen during the ash may give more efficient oxidation and removal of matrix components (46, 47) resulting in lower background absorption during atomize and permitting the use of lower ash temperatures. However, oxidation of the graphite tube will be much more rapid when oxygen is used.

When the graphite tube atomizer is programmed for a reduction of gas flow, the reduction is not instantaneous. It normally takes about one second for the flow through the atomizer to be reduced to zero. In most analyses, the delay in interruption of flow will not affect the analytical signal. When the atomization peak occurs within one second of the time at which the flow is reduced, the peak absorbance may be affected by the gas flow through the atomizer at the point of peak atom production. With volatile elements, such as cadmium or zinc, and in analyses where the maximum ash temperature is high relative to the temperature chosen for atomization, the peak atomization temperature will often be reached within one second or so of the start of the atomize ramp. In these cases, it will be necessary to compensate for the delay in gas reduction by inserting a step of appropriate length in the program prior to the atomize ramp to reduce the gas flow to the programmed value before the analyte atomization process begins.

The magnet is enabled when 'BC ON' mode is selected and is subsequently switched on by the 'read' command ('Yes' in the READ COMMAND column on the screen page for FURNACE PARAMETERS). The 'read' period determines the length of time for which the magnet is on and the instrument collects absorbance readings. It is preferable to set the 'read' period as short as is practicable to minimize the 'magnet on' period and in general the read command should be set for the beginning of the ramp to atomize temperature and continue as long as necessary to measure the peak. As noted earlier in this Chapter, care should be taken to ensure that there is no attenuation of the source light beam when the instrument 'read' begins. Examples of programs for the various elements are given in Chapter Four.

Interferences

Interferences in graphite tube atomizers may be physical, spectral or chemical in nature.

Chemical Interferences

Chemical interferences occurring when the ground-state population of atoms generated within the atomizer is altered as a result of interference by matrix components have been discussed in Chapter One. Chemical interferences can be alleviated to some extent by careful choice of ashing parameters to reduce the amount of matrix remaining at the start of atomization. Also, a chemical modifier can be used; see Chapter One for guidelines as to the best modifier to use for a particular analyte. Modifiers may be used both to stabilize the analyte, thus allowing higher ash temperatures, and to move the atomic signal away from the background signal, allowing more accurate background correction. Chemical interferences are often reduced by using higher atomization temperatures and platform atomization permits significant increases in atomization temperature for many elements. See references 301 and 303 for further discussion.

Physical Interferences

Physical interferences may result from differing behavior in the atomizer during the dry stage of samples of differing surface tension, viscosity or volume.

Vaporization of the analyte from different positions on the longitudinal axis of the graphite tube may affect the signal measured as a result of two factors:

The residence time of atoms will vary according to how far from the tube center the vaporization process occurs; atoms vaporizing near the end of the tube will have less distance to travel to escape the ends of the tube than atoms vaporized at the centre and this effect will be particularly noticeable with the inert gas stopped during atomize, since there will be no convective flow to force atoms out through the center hole of the tube.

A temperature gradient is present along graphite tubes used in electrothermal atomizers to a greater or lesser extent, depending on the design of the atomizer.

Samples of low surface tension, such as organic solvents, will spread in the tube to a greater extent than the equivalent volume of aqueous samples and this will also apply to solutions of differing viscosity. In addition, concentrated aqueous samples of acids may have a greater tendency to spread than dilute aqueous acids.

Naturally, larger volumes of the same solution will cover a larger portion of the inner surface of the tube. Provided that the sample is confined to the central portion of the tube during the dry, slight spreading will not affect the precision significantly. This is because the GTA tube is designed so that it is approximately isothermal over the central portion during both temperature ramp and hold steps. Matching of the physical properties of the sample to those of the standard is an important consideration in graphite furnace AA. The composition of the standards should match that of the samples when possible to minimize variations in properties such as surface tension and viscosity. The extent to which exact matching is necessary for a particular analysis will depend on the extent to which accuracy and precision are affected by variations in the sample composition. The extent to which matching is possible will depend on the analyst's knowledge of the solvent composition of the sample.

With many elements, there will be no significant difference in response between standards prepared in distilled water and those prepared in aqueous solutions containing several percent mineral acid. Differences in response with composition will become more likely with increasing concentration of acid. With high acid concentrations, it is possible to control the response by appropriate choice of the conditions for dry (see 'Selection of Temperature and Time Parameters' earlier in this Chapter). The dry conditions should be selected to give comparable desolvation behavior for standards and samples.

Further discussion of the matching of standards and samples is in Chapter Five.

The use of an automatic sampling device is preferred for sample injection, because of the better precision attainable with these devices in the positioning of the sample in the tube. When the autosampler is available as an accessory to the graphite tube atomizer, preparation of the calibration graph and sample analysis should be carried out by programming the autosampler to mix varying volumes of standard and sample solutions with blank to give the same total volume of solution, wherever possible. This procedure eliminates variation in the amount of spreading between samples of different volumes.

Problems arising from the retention of high viscosity samples in the sample dispensing device are usually overcome by correct injection technique, where micropipettes are used, and by dilution of high viscosity solutions (see also Chapter Five).

Background Absorption

Background absorption is usually due either to molecular absorption by salts which vaporize into the optical path or by scattering of light by particulate matter (49, 314, and 315). Light scattering is usually of small significance (314); broad-band absorption by molecular species is much the more significant and Figure 18 shows the variation in absorbance with wavelength for several halides of sodium (315); clearly, the absorption is significant over a considerable wavelength range.

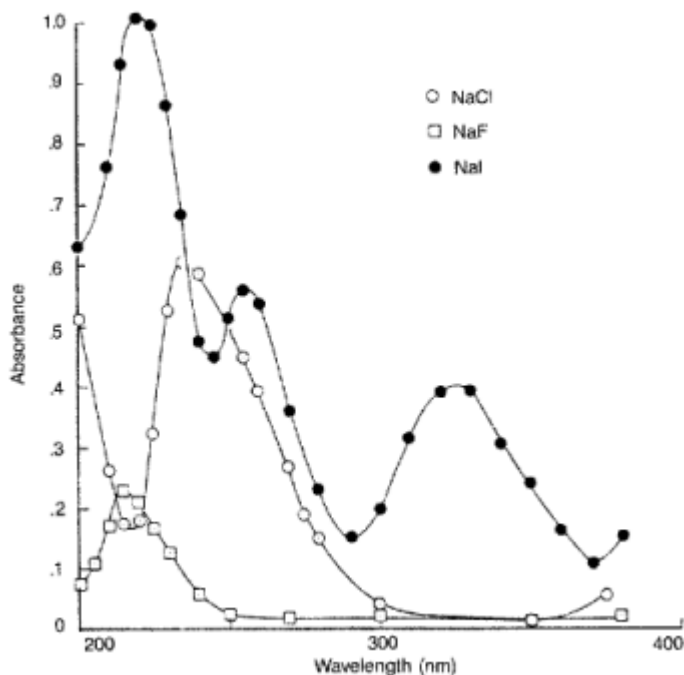


Figure 18. Molecular absorption spectra for halides

Mention has already been made of background correction using the Zeeman Effect and it has been emphasized that the Zeeman technique overcomes certain limitations of the continuum source technique viz. the Zeeman technique uses a single source, thus obviating the problems associated with aligning two lamps and that the correction is made exactly at the analytical wavelength. Nevertheless, small errors may remain; these residual errors are mainly due to the fact that the instrument has to cope with relatively low signal levels when the absorbance is high and the upper limit of background correction accuracy is set, in part, by the instrument electronics. For further discussion of this point see reference 50. The processing electronics of the SpectrAA system are designed so that even with a background absorbance of 2, the signals handled by the instrument processor are significantly higher than the inherent noise in the electronics.

The aim of the present chapter has been to present guidelines to help in the development of analytical programs which will lead to the most accurate and precise analytical results. Since most practical analyses involve samples that produce measurable background absorption during the atomization step, it is necessary to ensure that the conditions for accurate background correction are met.

In the first instance, a background overrange error signal on the DS-15 should indicate the presence of excessive background. Chemical modification of the sample or a higher ash temperature should then be tried. If the background is less than about 2.0 absorbance, the correction accuracy can be tested in two ways.

A simple method is to halve the volume of sample, which should contain analyte at a concentration to give an absorbance in the linear region of the calibration graph. See Chapter Four for examples of calibration graphs for each element showing the approximate linear range.

The background-corrected signal should also be halved. If it is not halved, the measurements provide evidence that background correction on the first sample is not accurate. See (48) for further discussion of this point.

Another method involves measuring the background-corrected signal at a nearby wavelength at which there is no atomic absorption. The hollow cathode lamp of another element can be used for this purpose and this should be as close to the wavelength of the analyte element as possible to ensure that the background is comparable at the two wavelengths. For example, in the determination of Cu at the 327.4 nm wavelength, the Ag line at 328.1 nm could be used. Deviations of the baseline should be not more than 2% of the background absorbance measured (0.02 absorbance for 1 absorbance peak background).

The first test is preferred because it is easier than the second, which may involve an additional lamp having significantly different noise characteristics to the analyte lamp.

If either test shows background correction problems, the answer may involve either reducing the background absorption (using a higher ash temperature or chemical modification) or moving the analyte signal away from the background signal (by chemical modification). The former course can also be effected by reducing the sample volume while a lower ramp rate can be used to reduce the background absorbance and separate the signals further.

As discussed in Chapter One, a rare type of spectral interference may arise in Zeeman atomic absorption with the magnetic field applied to the absorbing atoms where the lamp emission profile overlaps the absorption profile of a matrix element fine with the field on. This situation is manifested as an overcorrection and should be considered as a possible source of overcorrection errors. Further discussion is contained in references 289 and 290.

Incandescence

Under normal circumstances, light emitted by the walls of the furnace tube reaching the detector will not cause problems because this light, being continuous in nature, gives rise to a DC signal which is easily corrected by the instrument electronics. In less usual circumstances, it can happen that the emission from the furnace reaching the PM tube is so intense that the DC signal effectively 'floods' the detection/amplifier circuitry and a DC offset voltage cannot be applied to give accurate correction. In this case, a baseline movement corresponding to the error in correction may be observed. The emission intensity from the furnace can be described by the equations governing black-body radiation: the total intensity increases with temperature according to the Stefan-Boltzmann law, which the wavelength at which the intensity is maximum is also temperature-dependent. A furnace temperature of 2700 °C corresponds to a wavelength for maximum emission of approximately 1000 nm. However, the response of the photomultiplier tube as well as that of the monochromator show a wavelength dependence and the combination of these factors (actual emission intensity and instrumental response) has the consequence that the maximum photo current produced at the photomultiplier tube for a tube temperature of 2700 °C occurs at a wavelength of approximately 500 nm. (See Figure 19). The possibility of a contribution to the absorbance from tube emission is therefore strongest for elements with principal resonance lines lying in the region near 500 nm and which require high atomization temperatures. These elements include the rare earths such as Dy, Er, Eu and Tb but also the alkaline earths Ba and Ca.

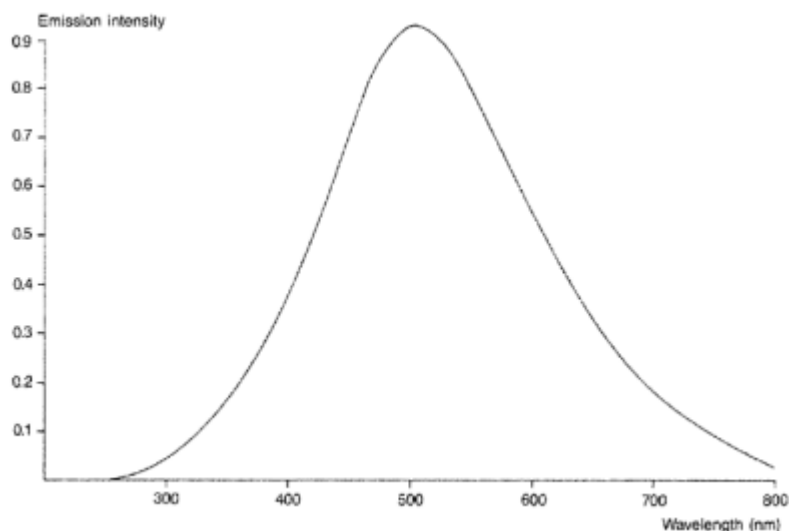
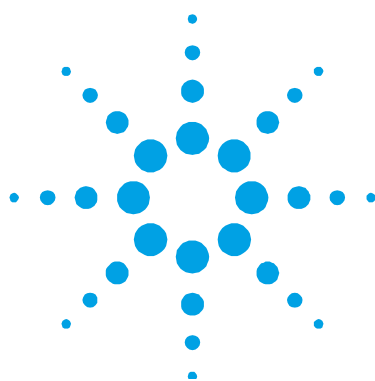


Figure 19. Apparent emission intensity vs. wavelength at 2700 °C

The atomizer should always be aligned to minimize the amount of emission from the tube reaching the PMT. This can usually be achieved by adjusting the furnace height for maximum hollow cathode light throughput. In addition, the reduced height slit should always be used for those elements requiring it. The furnace can then be fired (with no sample) to ensure that there is no baseline shift due to emission.

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4. Analytical Data

Notes and Definitions

The information in this chapter is intended as a guide in the selection of appropriate operating conditions for the Zeeman graphite tube atomizer. It is stressed that the data is applicable to analyte elements in simple matrices. Operating conditions for more complex samples will be different to some degree depending on the nature of the sample and the chemical form or state of the analyte element. For some elements data is presented for the pyrolytic platform atomizer as well as the graphite tube atomizer.

Whenever the sample differs significantly from the simple matrices quoted here, it will be essential to thoroughly investigate the behavior of the sample in the graphite tube atomizer so that optimum conditions can be established. Additional guidance for selection of operating parameters is given in Chapter Three; information about chemical modifiers will be found in Chapter One and Chapter Eight; the fundamentals of sample and standard preparation are discussed in Chapter Five.

Matrix

This is the matrix in which the element of interest was investigated.

Chemical Modifier

A chemical modifier is a reagent which when added to the sample either reduces interference, or isolates the analyte in a specific form that allows separation between background and analyte atomic absorption signals. An ideal chemical modifier is a reagent which not only reduces the background and interference effects, but also enhances the analyte sensitivity (see also Chapter One and Chapter Eight).

Furnace Operating Parameters

The analytical program from which the performance data was derived for a particular element in the specific matrix.

For the graphite tube:

- a** Steps 1 through 3 encompassed the Dry Stage.
- b** Steps 4 and 5 are the Ash Stage.
- c** Step 6 is the gas stop step.
- d** Step 7 is the 'ramp' step and Read Command.
- e** Step 8 is the Atomize 'hold' step and Read Command.
- f** Step 9 is a tube clean with maximum gas flow.

For the pyrolytic platform:

- a Steps 1 through 2 encompassed the Dry Stage.
- b Steps 3 and 4 are the Ash Stage.
- c Step 5 is the gas stop step.
- d Step 6 is the "ramp" step and Read Command.
- e Step 7 is the Atomize "hold" step and Read Command.
- f Step 8 is a tube clean with maximum gas flow.
- g Step 9 is a cool down step.

Dry Stage and Injected Volume

In obtaining the data presented in this chapter, a 20 μl volume was used throughout. Maximum gas flow (3.0 liters per minute) was used for the Dry Stage. Times and temperatures are those found to give best results for analyte elements in simple matrices. Note that correct drying technique is of fundamental importance in obtaining optimum analytical signal and maximum precision. Analysts may need to vary the drying times and temperatures depending on the characteristics of the sample being analyzed. The sample must be deposited consistently in the graphite tube or pyrolytic platform and dried evenly without loss. During method development, the sample droplet should be closely observed during the dry stage so that drying parameters can be correctly established.

Gas Stop, Ramp and Read Commands

For maximum sensitivity, gas flow should be off during the atomize steps. Whenever zero gas flow is required, for this purpose, it is necessary to include a step of 1 to 2 seconds duration at zero flow immediately before the atomize steps. This will ensure that the gas supply is completely turned off when the atomization stage begins (see also Chapter Three). The read command was commenced at the 'ramp' step and continued to the completion of atomization. All data was determined using a gas stop and maximum ramp rate, except for barium. This element has improved sensitivity in the graphite tube with a lower ramp rate.

Ash Stage

For other than simple matrices, a series of ashing steps will normally be required between Dry and Atomize. Ashing steps shown here for aqueous solutions would be modified significantly for complex samples. Where maximum sensitivity is required, the gas stop step will be implemented at the end of the ashing steps; the read command will commence on the 'ramp' step of the atomization stage. Specific programs including ashing steps and examples of setting ash parameters will be found in Chapter Seven.

Calibration

The recommended form of calibration for all elements is the injection of a fixed volume of varying concentrations. Standards can either be premixed, or they can be automatically made up by the sample dispenser using appropriate volumes of stock standard and blank (see Chapter Six).

In obtaining the calibration data presented in this chapter, a 20 μL volume was used throughout. When calibration is carried out by using different volumes, the response obtained with increasing volume should be checked against equivalent premixed standards to ensure that the calibration is analytically valid. The effect of varying the volumes of standard, blank and chemical modifiers should always be carefully studied (see Chapter Five).

The calibration must be established from standards which give peak Zeeman absorbances lower than the maximum absorbance (MAX ABS) specified for that wavelength and element.

AA Instrument Parameters

The AA Instrument Parameters were the recommended instrument conditions for the element of interest.

MAX. ABS

The maximum absorbance (MAX. ABS) is the maximum peak height Zeeman absorbance which can be used for the wavelength specified for the element, using a time constant of 0.05 seconds. All analytical measurements must be below this maximum peak absorbance. (See also Calibration Procedures in Chapter Five.)

An error message will appear if the peak analytical signal (including blank signal) is greater than the maximum absorbance stored for the particular element. Note that when peak area mode is used, it is the peak height absorbance which is governed by the MAX ABS limit.

If a time constant greater than 0.05 seconds or if another analytical wavelength is employed the maximum absorbance applicable to these conditions must be determined before proceeding.

The procedure for establishing MAX ABS is given under the heading 'Establishing A New Calibration' in Chapter Five.

MSR%

The MSR% (Magnetic Sensitivity Ratio) is the ratio of the Zeeman absorbance to the normal absorbance expressed as a percentage. Values are approximate and have been determined from normal absorbances ranging from 0.1 to 0.3.

The operation of the electromagnet is automatically linked to the read command to provide Zeeman background corrected absorbances.

Typical Characteristic Mass

The mass of an element which would typically yield an absorbance equal to 0.0044 absorbance (1% absorption) in the peak height mode, with a new pyrolytic coated graphite tube (or pyrolytic platform), under the Instrumental and Furnace Operating Parameters presented. All values have been determined with argon as the inert gas.

For the pyrolytic platform, the characteristic mass has also been determined from peak area measurements. It is the mass of an element which typically yields a signal equal to 0.0044 Abs.sec.

(1 ng = 10^{-9}g ; 1 pg = 10^{-12}g)

Maximum Ash Temperature

This is the recommended Maximum Ash Temperature for the matrix specified to avoid loss of analyte.

Typical Response

The Typical Response is the expected peak absorbance using the conditions listed and with new graphite components (pyrolytic coated tube or pyrolytic platform). A response within 25% of that quoted can be expected.

Inert Gas

The graphite tube atomizer allows operation with two gases. In compiling the data presented here, argon was used as the normal gas (designated NORMAL). Note that the normal gas (NORMAL) is also required for operation of the automatic sample dispenser.

Ag Atomic Number 47

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 400 | 5 | 3.0 | Normal | No |
| 5 | 400 | 1 | 3.0 | Normal | No |
| 6 | 400 | 2 | 0 | Normal | No |
| 7 | 2000 | 0.9 | 0 | Normal | Yes |
| 8 | 2000 | 2 | 0 | Normal | Yes |
| 9 | 2000 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 328.1 nm |
| Maximum Absorbance | 1.3 |
| MSR% | 97% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 338.3 | 0.5 |

Performance Data

Characteristic Mass (in argon): 0.7 pg

Maximum Ash Temperature: 500 °C

Recommended Chemical Modifiers

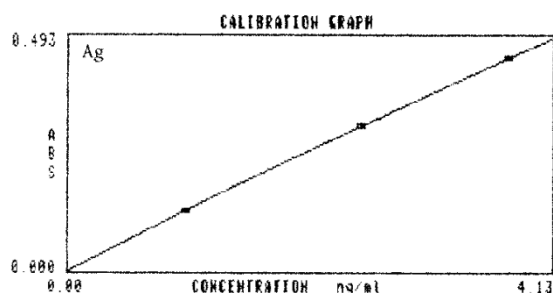
1% solution of ammonium dihydrogen orthophosphate.

or

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 3.5 ng/mL gives about 0.2 Abs.

The addition of either of these modifiers permits the use of a higher ashing temperature.

**Al** Atomic Number 13

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2500 | 0.8 | 0 | Normal | Yes |
| 8 | 2500 | 2 | 0 | Normal | Yes |
| 9 | 2500 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|-----------------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 396.2 nm, D ₂ 309.3 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 309.3 | 0.5 |
| 237.3 | 0.5 |
| 257.4 | 0.5 |
| 256.8 | 0.5 |

Performance Data

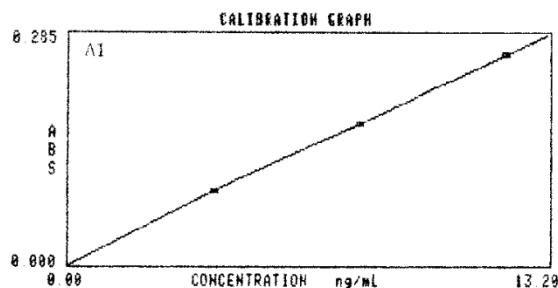
Characteristic Mass (in argon): 5 pg

Maximum Ash Temperature: 1400 °C

Typical Response (Argon): 10 µL of 25 ng/mL gives about 0.2 Abs.

An ash step at 1000 °C may be useful in obtaining a smooth peak shape.

The 309.3 line gives an MSR of 88% with a MAX ABS of 0.8, and a slightly poorer sensitivity than at 396.2 nm.



As Atomic Number 33

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

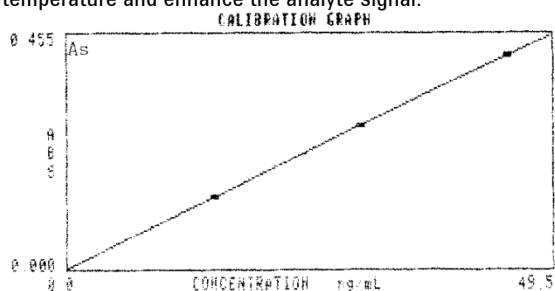
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1400 | 5 | 3.0 | Normal | No |
| 5 | 1400 | 1 | 3.0 | Normal | No |
| 6 | 1400 | 2 | 0 | Normal | No |
| 7 | 2600 | 0.6 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|-------------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2 nm, D ₂ 0.5 nm |
| Wavelength | 193.7 nm |
| Maximum Absorbance | 0.95 |
| MSR% | 86% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 197.2 | 1.0 |

Performance Data

Characteristic Mass (in argon): 10 µg*
Maximum Ash Temperature: 1500 °C*
Recommended Chemical Modifiers
Palladium solution (10 µL of 500 µg/mL)*
or
Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).
or
Nickel solution (50 µg/mL)
Typical Response (Argon): 10 µL of 50 ng/mL gives about 0.2 Abs.*
*Palladium modifier used to obtain these results.
The modifiers permit the use of a higher ashing temperature and enhance the analyte signal.



Au Atomic Number 79

Matrix 0.4% Hydrochloric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

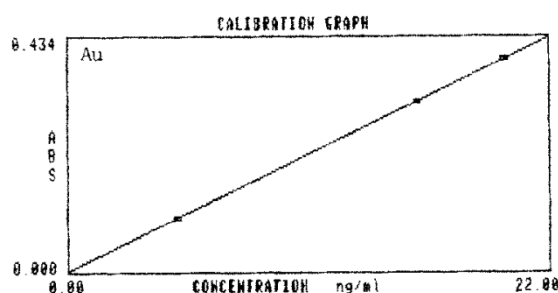
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 500 | 5 | 3.0 | Normal | No |
| 5 | 500 | 1 | 3.0 | Normal | No |
| 6 | 500 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 1.0 nm |
| Wavelength | 242.8 nm |
| Maximum Absorbance | 1.3 |
| MSR% | 94% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 267.6 | 1.0 |

Performance Data

Characteristic Mass (in argon): 4.4 µg
Maximum Ash Temperature: 7000 °C
Recommended Chemical Modifiers
Nickel nitrate 0.25% solution
or
Palladium solution (500- 2000 µg/mL) plus reducing agent such as ascorbic acid (368).
Typical Response (Argon): 10 µL of 22 ng/mL gives about 0.2 Abs.
The modifiers permit the use of a higher ashing temperature.
Standards were prepared in 0.4% hydrochloric acid from a gold (III) chloride standard solution .



B Atomic Number 5

Matrix 0.5% Hydrochloric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

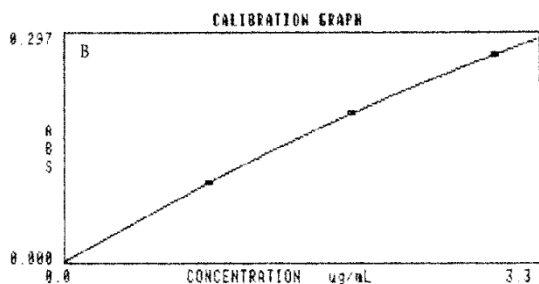
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 3000 | 1.4 | 0 | Normal | Yes |
| 8 | 3000 | 2 | 0 | Normal | Yes |
| 9 | 3000 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 20mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 249.8 nm |
| Maximum Absorbance | 0.45 |
| MSR% | 70% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 208.9 | 0.2 |

Performance Data

Characteristic Mass (in argon): 855 μg^*
Maximum Ash Temperature: 1000 °C
Recommended Chemical Modifiers
Lanthanum chloride or nitrate (100 $\mu\text{g}/\text{mL}$)
or Barium hydroxide (100 $\mu\text{g}/\text{mL}$)
Typical Response (Argon): 10 μL of 4300 ng/mL gives about 0.2 Abs.*
*Lanthanum chloride modifier used to obtain these results.
Boron was present as ortho-boric acid.
Both the lanthanum and barium hydroxide modifiers provide signal enhancement for boron.
Although the lanthanum modifier gives a background signal prior to atomization, a better response was obtained than when barium hydroxide was used (293).
Calcium hydroxide has also been used as a chemical modifier. Characteristic concentration without a chemical modifier can be three times poorer.

**Ba Atomic Number 56**

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

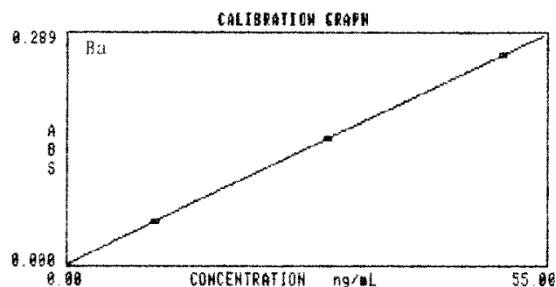
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2600 | 2.3 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 20mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 553.6 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 350.1 | 0.5 |

Performance Data

Characteristic Mass (in argon): 17 μg
Maximum Ash Temperature: 1400 °C
Typical Response (Argon): 10 μL of 85 ng/mL gives about 0.2 Abs.
Careful alignment of the furnace is essential (refer Chapter Three).
Contamination from the tube can be removed or greatly reduced by tube cleaning.
The best characteristic mass is obtained using an atomization ramp rate of 1000 °C/second.
At high absorbances slight upward curvature of the calibration has been observed



Be Atomic Number 4

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 10 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2300 | 0.7 | 0 | Normal | Yes |
| 8 | 2300 | 2 | 0 | Normal | Yes |
| 9 | 2300 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 1.0 nm |
| Wavelength | 234.9 nm |
| Maximum Absorbance | 0.7 |
| MSR% | 64% |

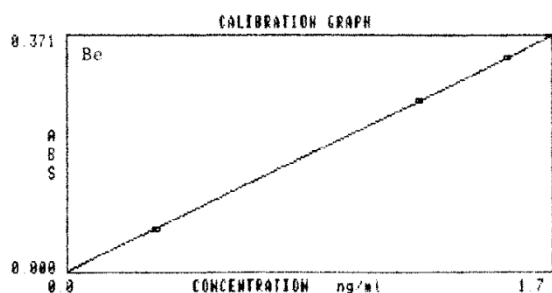
Performance Data

Characteristic Mass (in argon): 0.5 µg

Maximum Ash Temperature: 1000 °C

Typical Response (Argon): 10 µL of 2.5 ng/mL gives about 0.2 Abs.

Improved reproducibility of peak shape was obtained by using an ash stage at 1000 °C.

**Bi** Atomic Number 83

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 400 | 5 | 3.0 | Normal | No |
| 5 | 400 | 1 | 3.0 | Normal | No |
| 6 | 400 | 2 | 0 | Normal | No |
| 7 | 2000 | 0.8 | 0 | Normal | Yes |
| 8 | 2000 | 2 | 0 | Normal | Yes |
| 9 | 2000 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|-------------------------------|
| Lamp Current | 10mA |
| Spectral Bandwidth | 0.1 nm, D ₂ 0.2 nm |
| Wavelength | 223.1 nm |
| Maximum Absorbance | 1.5 |
| MSR% | 88% |

| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
|------------------------------|--------------------------|
| 306.8 | 0.5 |
| 227.7 | 0.5 |

Performance Data

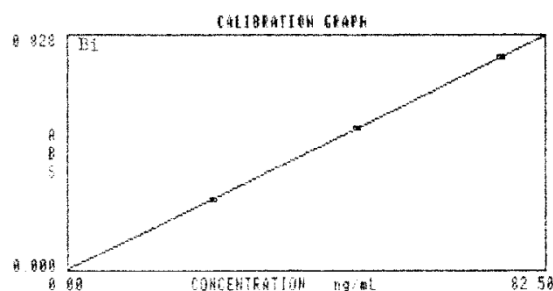
Characteristic Mass (in argon): 9 µg

Maximum Ash Temperature: 500 °C

Recommended Chemical Modifiers

Palladium or nickel (1000 µg/mL),

Typical Response (Argon): 10 µL of 45 ng/mL gives about 0.2 Abs.



Ca Atomic Number 20

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 422.7 nm |
| Maximum Absorbance | 2 |
| MSR% | 94% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 239.9 | 0.2 |

Performance Data

Characteristic Mass (in argon): 0.6 µg

Maximum Ash Temperature: 1200 °C

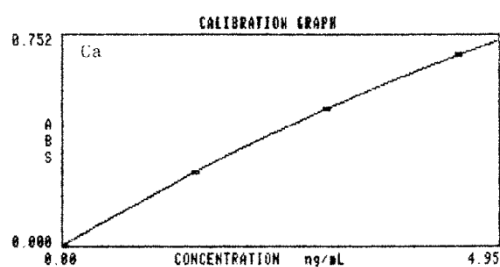
Typical Response (Argon): 10 µL of 3 ng/mL gives about 0.2 Abs.

Improved reproducibility of peak shape was obtained by using an ash stage at 1000 °C.

Determinations for calcium are very sensitive; calcium may be found in most natural substances. Before starting any calcium determinations perform the following:

1. Clean the graphite tube (3-5 operations of the Tube Clean).
2. Determine the level of contamination from the reagents by measuring a representative blank.
3. Determine any residual levels in the graphite tube after cleaning by operating the furnace program without samples, standards or blank.

Careful alignment of the furnace is essential (refer to Chapter Three).

**Cd** Atomic Number 48

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 250 | 5 | 3.0 | Normal | No |
| 5 | 250 | 1 | 3.0 | Normal | No |
| 6 | 250 | 2 | 0 | Normal | No |
| 7 | 1800 | 0.8 | 0 | Normal | Yes |
| 8 | 1800 | 2 | 0 | Normal | Yes |
| 9 | 1800 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 228.8 nm |
| Maximum Absorbance | 0.7 |
| MSR% | 87% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 326.1 | 0.5 |

Performance Data

Characteristic Mass (in argon): 2 µg*

Maximum Ash Temperature: 300 °C

Recommended Chemical Modifiers

Monobasic ammonium phosphate (5000 µg/mL solution)* or Orthophosphoric acid (1000 µg/mL)

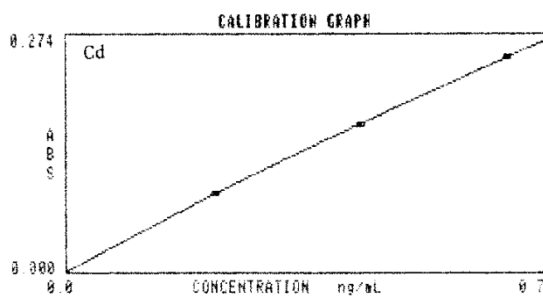
or Palladium solution (500-2000 µg/mL) plus a reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 1.1 ng/mL gives about 0.2 Abs.*

*The ammonium phosphate modifier was used to obtain these results.

The monobasic ammonium phosphate modifier ensures a smooth peak shape and allows a maximum ash of 600 °C (293).

The palladium chemical modifier permits the use of a higher ashing temperature.



Co **Atomic Number 27**

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

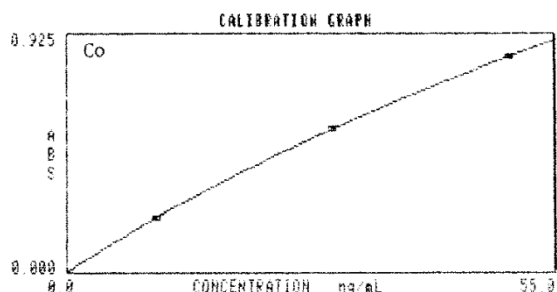
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 750 | 5 | 3.0 | Normal | No |
| 5 | 750 | 1 | 3.0 | Normal | No |
| 6 | 750 | 2 | 0 | Normal | No |
| 7 | 2300 | 1.1 | 0 | Normal | Yes |
| 8 | 2300 | 2 | 0 | Normal | Yes |
| 9 | 2300 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|-----------------------------------|
| Lamp Current | 7 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 242.5 nm, D ₂ 240.7 nm |
| Maximum Absorbance | 1.1 |
| MSR% | 98% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 240.7 | 0.2 |
| 304.4 | 0.5 |
| 346.6 | 0.2 |

Performance Data

Characteristic Mass (in argon): 4.2 µg
Maximum Ash Temperature: 900 °C
Recommended Chemical Modifiers
Palladium solution (500-2000 µg/mL) plus a reducing agent such as ascorbic acid (368).
Typical Response (Argon): 10 µL of 21 ng/mL gives about 0.2 Abs.
The 240.7 nm line for cobalt gives an MSR of 85% and a MAX. ABS of 0.6 with a slightly better sensitivity than the 242.5 nm line.
The chemical modifier permits the use of a higher ashing temperature.



Cr **Atomic Number 24**

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

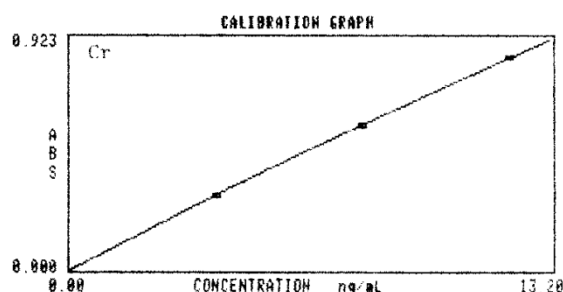
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 7 mA |
| Spectral Bandwidth | 0.2R nm |
| Wavelength | 357.9 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 429.0 | 0.5 |
| 520.8 | 0.2 |
| 520.5 | 0.2 |

Performance Data

Characteristic Mass (in argon): 1.5 µg
Maximum Ash Temperature: 1100 °C
Recommended Chemical Modifiers
Palladium solution (500-2000 µg/mL) plus a reducing agent such as ascorbic acid (368).
Typical Response (Argon): 10 µL of 7.5 ng/mL gives about 0.2 Abs.
The chemical modifier permits the use of a higher ashing temperature.



Cs Atomic Number 55

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 500 | 5 | 3.0 | Normal | No |
| 5 | 500 | 1 | 3.0 | Normal | No |
| 6 | 500 | 2 | 0 | Normal | No |
| 7 | 2200 | 0.9 | 0 | Normal | Yes |
| 8 | 2200 | 2 | 0 | Normal | Yes |
| 9 | 2200 | 2 | 3.0 | Normal | No |

Instrument Parameters

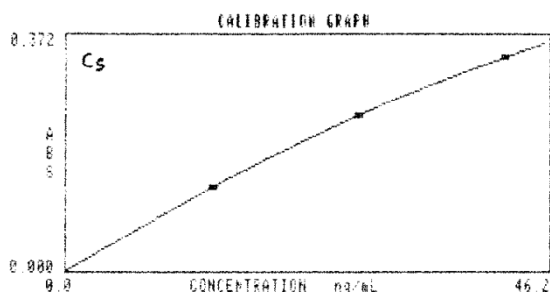
| | |
|------------------------------|--------------------------|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 1.0R nm |
| Wavelength | 852.1 nm |
| Maximum Absorbance | 0.9 |
| MSR% | 58% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 455.5 | 0.5 |

Performance Data

Characteristic Mass (in argon): 11 pg

Maximum Ash Temperature: 600 °C

Typical Response (Argon): 10 µL of 55 ng/mL gives about 0.2 Abs.

**Cu Atomic Number 29**

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 800 | 5 | 3.0 | Normal | No |
| 5 | 800 | 1 | 3.0 | Normal | No |
| 6 | 800 | 2 | 0 | Normal | No |
| 7 | 2300 | 1.1 | 0 | Normal | Yes |
| 8 | 2300 | 2 | 0 | Normal | Yes |
| 9 | 2300 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|----------------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 327.4 nm, D ₂ 324.8nm |
| Maximum Absorbance | 1.6 |
| MSR% | 84% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 324.8 | 0.5 |
| 217.9 | 0.2 |
| 218.2 | 0.2 |
| 222.6 | 0.2 |
| 244.2 | 1.0 |

Performance Data

Characteristic Mass (in argon): 6 pg

Maximum Ash Temperature: 900 °C

Recommended Chemical Modifiers

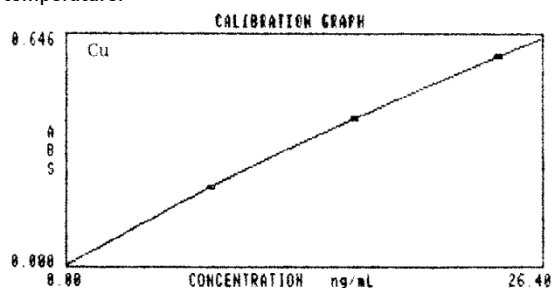
Palladium solution (500-2000 µg/mL) plus a reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 30 ng/mL gives about 0.2 Abs.

The 324.8 nm wavelength for Cu gives an MSR of 64% and a MAX. ABS of 0.8, with a slightly better sensitivity than the 327.4 nm line.

Improved linearity is obtained with the 327.4 line.

The chemical modifier permits the use at a higher ashing temperature.



Dy Atomic Number 66

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2900 | 1.4 | 0 | Normal | Yes |
| 8 | 2900 | 2 | 0 | Normal | Yes |
| 9 | 2900 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 0.2R nm |
| Wavelength | 421.2 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 419.5 | 0.2 |

Performance Data

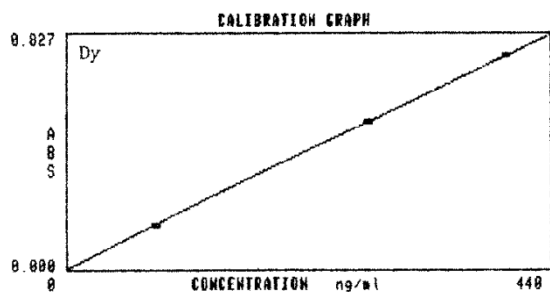
Characteristic Mass (in argon): 45 pg

Maximum Ash Temperature: 1200 °C

Typical Response (Argon): 10 µL of 225 ng/mL gives about 0.2 Abs.

The slight memory associated with dysprosium, especially at atomization temperatures lower than 2900 °C, can be eliminated by incorporating a higher temperature tube cleaning step after the atomize stage.

Careful alignment of the graphite tube atomizer is necessary to reduce possible emission from the tube (refer Chapter Three).

**Er** Atomic Number 68

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 400.8 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 389.3 | 0.5 |
| 408.8 | 0.2 |
| 402.1 | 0.2 |

Performance Data

Characteristic Mass (in argon): 100 pg

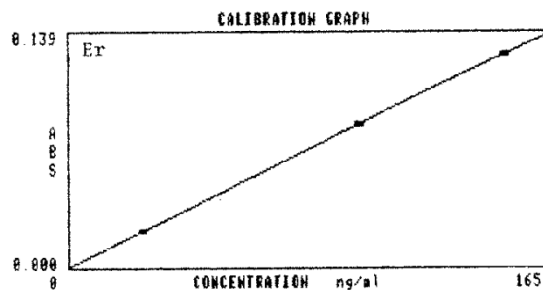
Maximum Ash Temperature: 1200 °C

Typical Response (Argon): 10 µL of 500 ng/mL gives about 0.2 Abs.

Careful alignment of the graphite tube atomizer is necessary to reduce possible emission from the tube (refer Chapter Three).

A memory effect has been observed which can be eliminated by using a higher temperature step after the atomize stage to clean the tube.

At high absorbances slight upward curvature of the calibration has been observed.



Eu Atomic Number 63

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2500 | 1.3 | 0 | Normal | Yes |
| 8 | 2500 | 2 | 0 | Normal | Yes |
| 9 | 2500 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 1.0R nm |
| Wavelength | 459.4 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 333.4 | 0.5 |

Performance Data

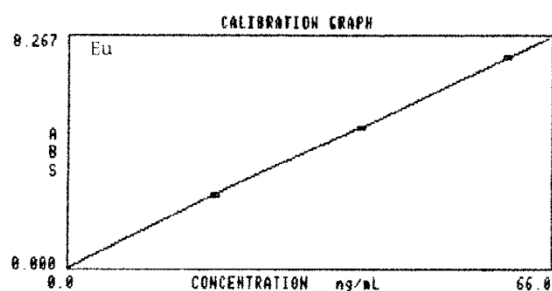
Characteristic Mass (in argon): 25 pg

Maximum Ash Temperature: 1100 °C

Typical Response (Argon): 10 µL of 125 ng/mL gives about 0.2 Abs.

Careful alignment of the graphite tube atomizer is necessary to reduce possible emission from the tube (refer Chapter Three).

At high absorbances slight upward curvature of the calibration has been observed.

**Fe Atomic Number 26**

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2300 | 1.1 | 0 | Normal | Yes |
| 8 | 2300 | 2 | 0 | Normal | Yes |
| 9 | 2300 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 248.3 nm |
| Maximum Absorbance | 0.9 |
| MSR% | 97% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 372.0 | 0.2 |
| 386.0 | 0.2 |

Performance Data

Characteristic Mass (in argon): 1.2 pg

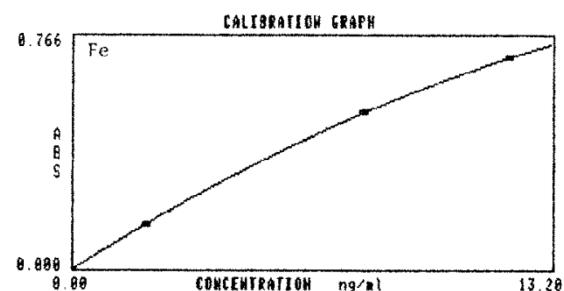
Maximum Ash Temperature: 800 °C

Recommended Chemical Modifiers

Palladium solution (500-2000 µg/mL) plus a reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 6 ng/mL gives about 0.2 Abs.

The chemical modifier permits the use of a higher ashing temperature.



Ga Atomic Number 31

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 500 | 5 | 3.0 | Normal | No |
| 5 | 500 | 1 | 3.0 | Normal | No |
| 6 | 500 | 2 | 0 | Normal | No |
| 7 | 2500 | 1.2 | 0 | Normal | Yes |
| 8 | 2500 | 2 | 0 | Normal | Yes |
| 9 | 2500 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 294.4 nm |
| Maximum Absorbance | 0.7 |
| MSR% | 80% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 287.4 | 0.5 |
| 272.0 | 0.5 |

Performance Data

Characteristic Mass (in argon): 4.5 µg*

Maximum Ash Temperature: 600 °C

Recommended Chemical Modifiers

Palladium (5 µL of 100 µg/mL) or

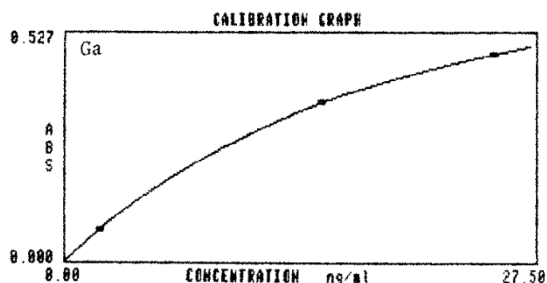
Nickel nitrate (1 mg/mL)

Typical Response (Argon): 10 µL of 22 ng/mL gives about 0.2 Abs.*

*Palladium modifier used to obtain these results.

The use of either nickel nitrate or a palladium solution as a chemical modifier for Ga increases the sensitivity and permits the use of a higher ashing temperature.

The 287.4 nm line for Ga gives an MSR of 71%, a MAX ABS of 1.0 and a sensitivity approximately the same as the 294.4 nm line.

**Ge** Atomic Number 32

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.3 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 1.0 nm |
| Wavelength | 265.2 nm |
| Maximum Absorbance | 1.6 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 269.1 | 0.5 |
| 303.9 | 0.5 |

Performance Data

Characteristic Mass (in argon): 9 µg*

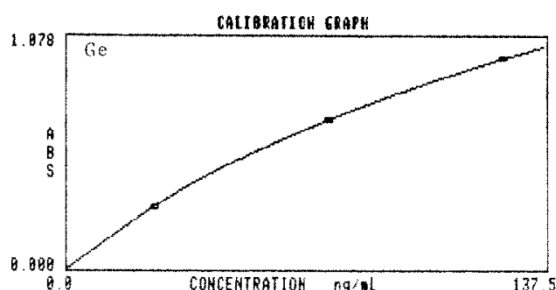
Maximum Ash Temperature: 800 °C

Recommended Chemical Modifiers

Palladium (5 µL of 100 µg/mL)

Typical Response (Argon): 10 µL of 45 ng/mL gives about 0.2 Abs.*

*Palladium modifier used to obtain these results. The use of palladium as a modifier for germanium allows the use of higher ashing temperatures and improves sensitivity.



Hg Atomic Number 80

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 200 | 5 | 3.0 | Normal | No |
| 5 | 200 | 5 | 3.0 | Normal | No |
| 6 | 200 | 2 | 0 | Normal | No |
| 7 | 1800 | 0.8 | 0 | Normal | Yes |
| 8 | 1800 | 2 | 0 | Normal | Yes |
| 9 | 1800 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 253.7 nm |
| Maximum Absorbance | 0.35 |
| MSR% | 69% |

Performance Data

Characteristic Mass (in argon): 150 pg*

Maximum Ash Temperature: 500 °C

Recommended Chemical Modifiers

Palladium solution (1000 µg/mL)* or

Palladium solution (500-2000 µg/mL) plus a reducing agent such as ascorbic acid (368) or

Diammonium sulphide in excess

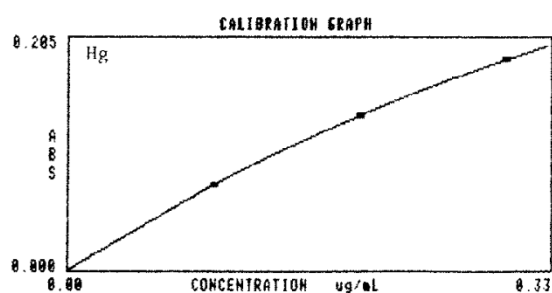
Typical Response (Argon): 10 µL of 750 ng/mL gives about 0.2 Abs.*

*Pd modifier used to obtain these results. The palladium modifier is pre-injected and taken to step 3.

The palladium modifier permits the use of a higher ashing temperature and enhances the signal.

The diammonium sulphide modifier stabilized the mercury signal.

Fresh dilutions of the mercury standards should be prepared each day as the standards are not very stable.

**In** Atomic Number 49

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 600 | 5 | 3.0 | Normal | No |
| 5 | 600 | 1 | 3.0 | Normal | No |
| 6 | 600 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|-----------------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 325.6 nm, D ₂ 303.9 nm |
| Maximum Absorbance | 1.6 |
| MSR% | 100% |

Performance Data

Characteristic Mass (in argon): 7.0 pg*

Maximum Ash Temperature: 700 °C

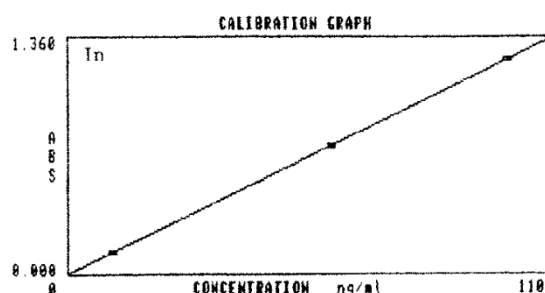
Recommended Chemical Modifiers

Palladium solution (5 µL of 1 mg/mL)

Typical Response (Argon): 10 µL of 35 ng/mL gives about 0.2 Abs.*

*Palladium modifier used to obtain these results. The use of palladium as a chemical modifier for indium, allows the use of higher ashing temperatures, and improves sensitivity.

The 303.9 nm line for indium has a low MSR%.



Ir Atomic Number 77

Matrix 0.2% Hydrochloric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2900 | 1 | 0 | Normal | Yes |
| 8 | 2900 | 2 | 0 | Normal | Yes |
| 9 | 2900 | 1 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|---|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 264.0 nm, D ₂ 208.9 nm (0.2) |
| Maximum Absorbance | 0.9 |
| MSR% | 97% |

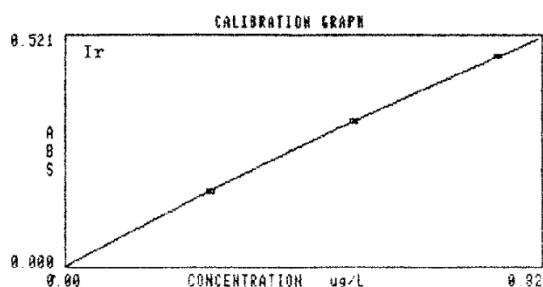
Performance Data

Characteristic Mass (in argon): 135 pg

Maximum Ash Temperature: 1000 °C

Recommended Chemical Modifiers

Typical Response (Argon): 10 µL of 610 ng/mL gives about 0.2 Abs.

**K** Atomic Number 19

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2100 | 1 | 0 | Normal | Yes |
| 8 | 2100 | 2 | 0 | Normal | Yes |
| 9 | 2100 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 1.0R nm |
| Wavelength | 766.5 nm |
| Maximum Absorbance | 2 |
| MSR% | 90% |

| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
|------------------------------|--------------------------|
| 769.9 | 1.0 |
| 404.4 | 0.5 |

Performance Data

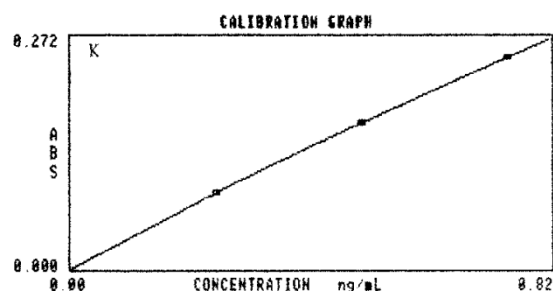
Characteristic Mass (in argon): 0.4 pg

Maximum Ash Temperature: 800 °C

Typical Response (Argon): 10 µL of 2 ng/mL gives about 0.2 Abs.

Determinations for potassium are very sensitive; potassium is a common contaminant in water and reagents.

At high absorbances, slight upward curvature of the calibration has been observed.



Li Atomic Number 3

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2300 | 1.1 | 0 | Normal | Yes |
| 8 | 2300 | 2 | 0 | Normal | Yes |
| 9 | 2300 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 1.0R nm |
| Wavelength | 670.8 nm |
| Maximum Absorbance | 1.4 |
| MSR% | 49% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 323.3 | 0.2 |
| 610.4 | 0.5 |

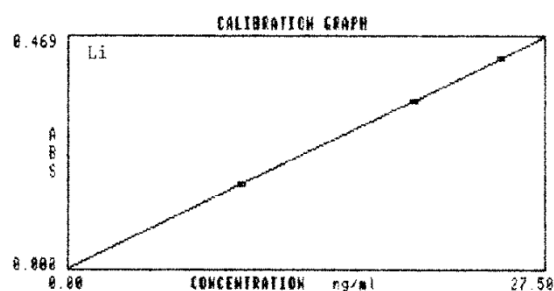
Performance Data

Characteristic Mass (in argon): 4 pg

Maximum Ash Temperature: 800 °C

Typical Response (Argon): 10 µL of 20 ng/mL gives about 0.2 Abs.

At high absorbances, slight upward curvature of the calibration has been observed.

**Mg** Atomic Number 12

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 900 | 5 | 3.0 | Normal | No |
| 5 | 900 | 1 | 3.0 | Normal | No |
| 6 | 900 | 2 | 0 | Normal | No |
| 7 | 2200 | 1 | 0 | Normal | Yes |
| 8 | 2200 | 2 | 0 | Normal | Yes |
| 9 | 2200 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 285.2 nm |
| Maximum Absorbance | 0.55 |
| MSR% | 75% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 202.5 | 1.0 |

Performance Data

Characteristic Mass (in argon): 0.2 pg

Maximum Ash Temperature: 900 °C

Typical Response (Argon): 10 µL of 1 ng/mL gives about 0.2 Abs.

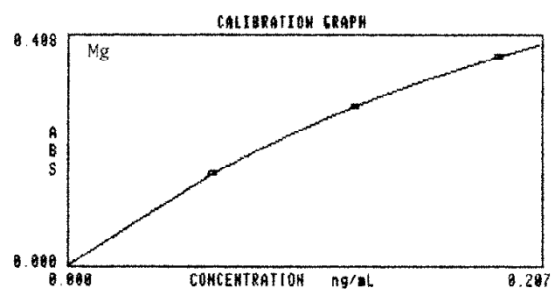
An ash step at 900 °C may be useful in obtaining a smooth peak shape.

Determinations for magnesium are very sensitive; magnesium is a common contaminant in water and reagents.

Before any magnesium determinations are made, it is essential to perform the following:

1. Clean the graphite tube (3-5 operations of the Tube Clean).
2. Determine the level of contamination from reagents by measuring a representative blank.
3. Determine any residual levels in the graphite tube after cleaning by operating the furnace program without samples, standards or blanks.

A lower lamp current may be used to obtain a higher MAX ABS.



Mn Atomic Number 25

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2400 | 1.1 | 0 | Normal | Yes |
| 8 | 2400 | 2 | 0 | Normal | Yes |
| 9 | 2400 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 279.5 nm |
| Maximum Absorbance | 1.2 |
| MSR% | 92% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 403.1 | 0.2 |
| 321.7 | 0.2 |

Performance Data

Characteristic Mass (in argon): 0.6 pg

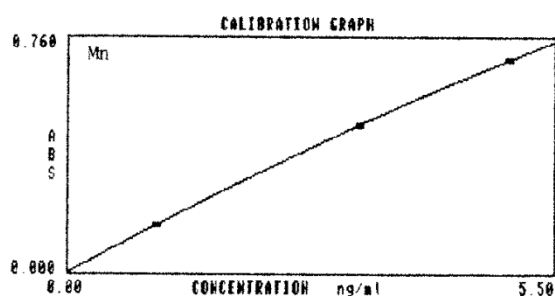
Maximum Ash Temperature: 800 °C

Recommended Chemical Modifiers

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 3 ng/mL gives about 0.2 Abs.

The chemical modifier permits the use of a higher ashing temperature.

**Mo** Atomic Number 42

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2800 | 1.3 | 0 | Normal | Yes |
| 8 | 2800 | 2 | 0 | Normal | Yes |
| 9 | 2800 | 2 | 3.0 | Normal | No |

Instrument Parameters

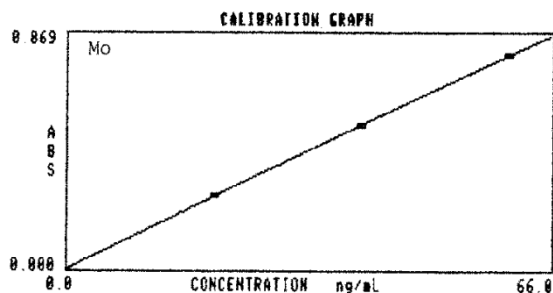
| | |
|------------------------------|--------------------------|
| Lamp Current | 7 mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 313.3 nm |
| Maximum Absorbance | 2 |
| MSR% | 96% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 320.9 | 0.2 |

Performance Data

Characteristic Mass (in argon): 7 pg

Maximum Ash Temperature: 1200 °C

Typical Response (Argon): 10 µL of 35 ng/mL gives about 0.2 Abs.



Na Atomic Number 11

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2000 | 0.9 | 0 | Normal | Yes |
| 8 | 2000 | 2 | 0 | Normal | Yes |
| 9 | 2000 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.2R nm |
| Wavelength | 589.6 nm |
| Maximum Absorbance | 1.5 |
| MSR% | 92% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 589.0 | 0.2 |
| 330.3 | 0.5 |

Performance Data

Characteristic Mass (in argon): 0.1 µg

Maximum Ash Temperature: 800 °C

Typical Response (Argon): 10 µL of 0.5 ng/mL gives about 0.2 Abs.

The chemical modifier permits the use of a higher ashing temperature.

Determinations for sodium by graphite furnace AA are very sensitive. Sodium is a common contaminant and high levels may be found in waters, reagents and the laboratory environment.

Before starting a sodium determination:

1. Clean the graphite tube (3-5 operations of the Tube Clean)
2. Determine the level of contamination from reagents by measuring a representative blank.
3. Determine any residual levels in the graphite tube after cleaning by operating the furnace program without standards, samples or blanks.

A clean room environment is necessary to determine trace levels of sodium by graphite furnace AA as the technique is extremely sensitive. Flame AA is recommended for the analysis of higher levels of sodium.

Although the 589.0 nm line for sodium is more sensitive (by a factor of 2) than the 589.6 nm line, the latter is recommended as it exhibits greater linearity.

Ni Atomic Number 28

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 800 | 5 | 3.0 | Normal | No |
| 5 | 800 | 1 | 3.0 | Normal | No |
| 6 | 800 | 2 | 0 | Normal | No |
| 7 | 2400 | 1.1 | 0 | Normal | Yes |
| 8 | 2400 | 2 | 0 | Normal | Yes |
| 9 | 2400 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 232.0 nm |
| Maximum Absorbance | 1.0 |
| MSR% | 98% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 352.5 | 0.5 |
| 351.5 | 0.5 |
| 362.5 | 0.2 |

Performance Data

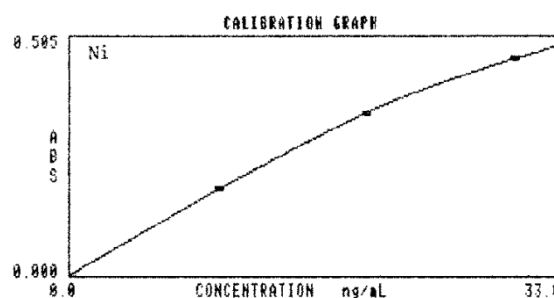
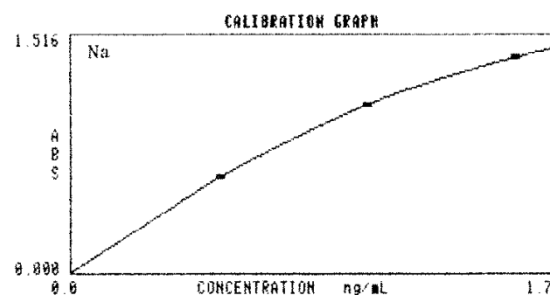
Characteristic Mass (in argon): 4.8 µg

Maximum Ash Temperature: 900 °C

Recommended Chemical Modifiers

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 24 ng/mL gives about 0.2 Abs. The chemical modifier permits the use of a higher ashing temperature.



P Atomic Number 15

Matrix Phosphoric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2700 | 1 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 1.0 nm |
| Wavelength | 213.6 nm |
| Maximum Absorbance | 0.65 |
| MSR% | 69% |

Performance Data

Characteristic Mass (in argon): 2200 pg*

Maximum Ash Temperature: 800 °C

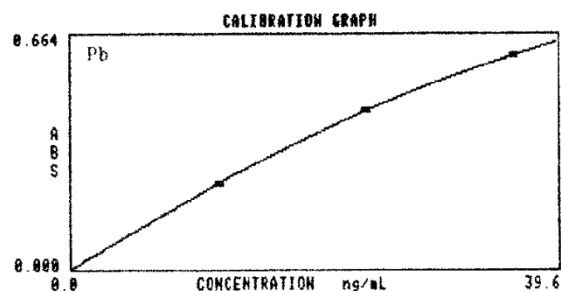
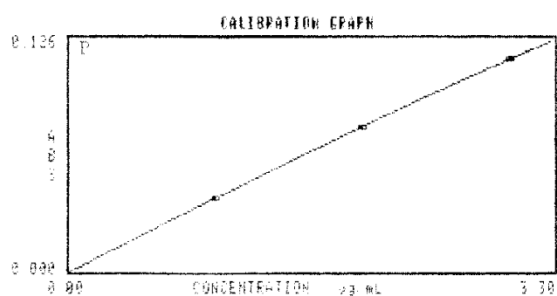
Recommended Chemical Modifiers

Lanthanum solution (5 µL of 1000 µg/mL)* or

Nickel solution (0.2% as nitrate)

Typical Response (Argon): 10 µL of 11 ng/mL gives about 0.2 Abs.*

*Lanthanum modifier used to obtain these results.

**Pb** Atomic Number 82

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 400 | 5 | 3.0 | Normal | No |
| 5 | 400 | 1 | 3.0 | Normal | No |
| 6 | 400 | 2 | 0 | Normal | No |
| 7 | 2100 | 1 | 0 | Normal | Yes |
| 8 | 2100 | 2 | 0 | Normal | Yes |
| 9 | 2100 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 283.3 nm |
| Maximum Absorbance | 1.4 |
| MSR% | 92% |

| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
|------------------------------|--------------------------|
| 217.0 | 1.0 |
| 261.4 | 0.5 |

Performance Data

Characteristic Mass (in argon): 5.5 pg

Maximum Ash Temperature: 600 °C

Recommended Chemical Modifiers

Orthophosphoric acid (1000 µg/mL) or

Ammonium dihydrogen orthophosphate (5 mg/mL) or

EDTA, citrate, oxalate (0.5 – 1% v/v) – See Chapter One or

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 27 ng/mL gives about 0.2 Abs.

Phosphate chemical modifiers permit the use of a higher ashing temperature and stabilize the lead signal.

The use of EDTA, citrate or oxalate stabilizes the lead allowing it to atomize at a lower temperature than does a nitrate or chloride matrix.

The palladium chemical modifier permits the use of a higher ashing temperature.

Lead is a common contaminant in reagents and it is essential that a representative blank is measured before proceeding with the analytical program.

The atomization temperature can be altered by chemical modifiers. The chemical matrix plays an important role in determining optimum ash and atomizing conditions. It is strongly recommended that the ash steps be extensively investigated.

Non-atomic absorption may be higher at the 217.0 nm line, for which the MAX. ABS is 0.6 and the MSR is 71%.

Pd Atomic Number 46

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2500 | 1.2 | 0 | Normal | Yes |
| 8 | 2500 | 2 | 0 | Normal | Yes |
| 9 | 2500 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 244.8 nm |
| Maximum Absorbance | 0.9 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 247.6 | 0.2 |
| 340.5 | 1.0 |

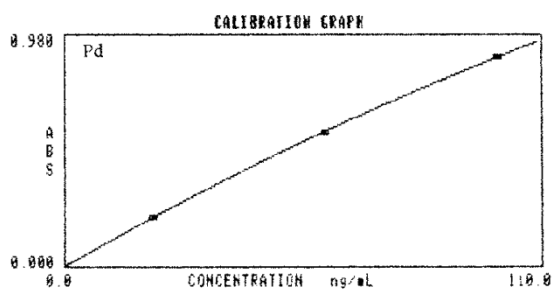
Performance Data

Characteristic Mass (in argon): 8.6 pg

Maximum Ash Temperature: 1100 °C

Typical Response (Argon): 10 µL of 43 ng/mL gives about 0.2 Abs.

The 247.6 nm line has an MSR of approximately 100%, a MAX ABS of 1.4 and a slightly poorer sensitivity (by about 20%). It could be the preferred line for some analyses because of the extended calibration range.

**Pt** Atomic Number 78

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

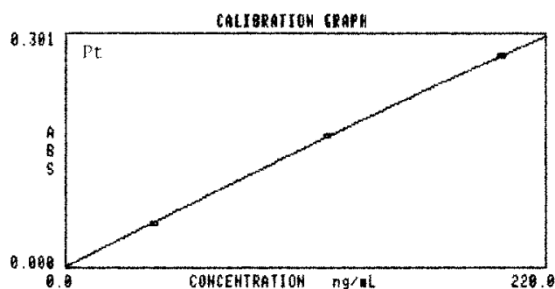
| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 265.9 nm |
| Maximum Absorbance | 1.1 |
| MSR% | 82% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 299.8 | 0.5 |

Performance Data

Characteristic Mass (in argon): 70 pg

Maximum Ash Temperature: 1200 °C

Typical Response (Argon): 10 µL of 350 ng/mL gives about 0.2 Abs.



Rb Atomic Number 37

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

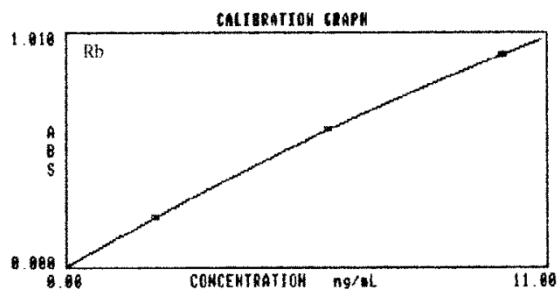
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 500 | 5 | 3.0 | Normal | No |
| 5 | 500 | 1 | 3.0 | Normal | No |
| 6 | 500 | 2 | 0 | Normal | No |
| 7 | 2000 | 0.9 | 0 | Normal | Yes |
| 8 | 2000 | 2 | 0 | Normal | Yes |
| 9 | 2000 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 0.2R nm |
| Wavelength | 780.0 nm |
| Maximum Absorbance | 2 |
| MSR% | 90% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 794.8 | 0.2 |
| 420.2 | 0.2 |
| 421.6 | 0.2 |

Performance Data

Characteristic Mass (in argon): 1 pg
Maximum Ash Temperature: 600 °C
Typical Response (Argon): 10 µL of 5 ng/mL gives about 0.2 Abs.
At high absorbances slight upward curvature of the calibration has been observed.



Rh Atomic Number 45

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

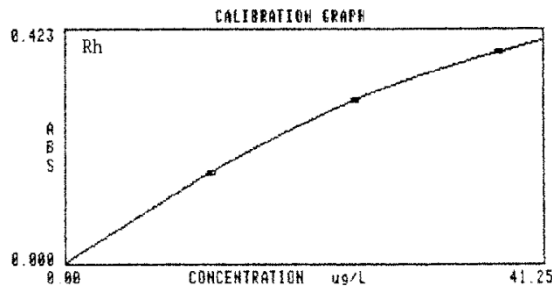
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 900 | 5 | 3.0 | Normal | No |
| 5 | 900 | 1 | 3.0 | Normal | No |
| 6 | 900 | 2 | 0 | Normal | No |
| 7 | 2850 | 1 | 0 | Normal | Yes |
| 8 | 2850 | 2 | 0 | Normal | Yes |
| 9 | 2850 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 343.5 nm |
| Maximum Absorbance | 0.6 |
| MSR% | 95% |

Performance Data

Characteristic Mass (in argon): 8 pg
Maximum Ash Temperature: 1000 °C
Typical Response (Argon): 10 µL of 37 ng/mL gives about 0.2 Abs.



Ru Atomic Number 44

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2R nm |
| Wavelength | 349.9 nm |
| Maximum Absorbance | 1.4 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 392.6 | 0.2 |

Performance Data

Characteristic Mass (in argon): 15 pg

Maximum Ash Temperature: 1200 °C

Typical Response (Argon): 10 µL of 75 ng/mL gives about 0.2 Abs.

Sb Atomic Number 51

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2000 | 0.7 | 0 | Normal | Yes |
| 8 | 2000 | 2 | 0 | Normal | Yes |
| 9 | 2000 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 217.6 nm |
| Maximum Absorbance | 1.4 |
| MSR% | 96% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 231.2 | 0.5 |

Performance Data

Characteristic Mass (in argon): 10 pg

Maximum Ash Temperature: 800 °C

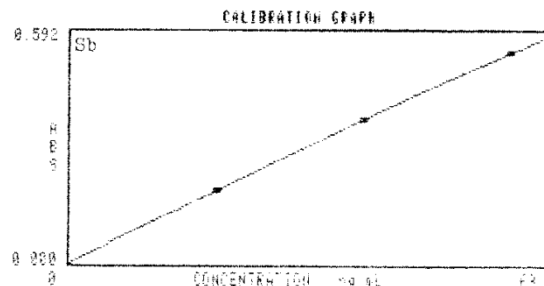
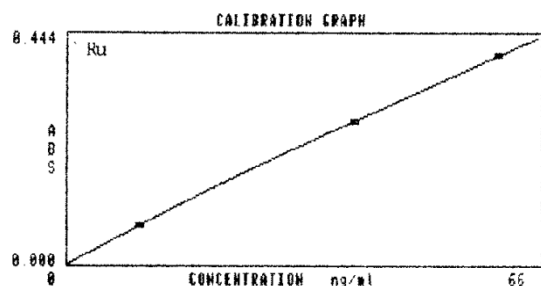
Recommended Chemical Modifiers

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368) or

Nickel nitrate solution (50-1000 µg/mL)

Typical Response (Argon): 10 µL of 50 ng/mL gives about 0.2 Abs.

The modifiers permit the use of a higher ashing temperature and enhance the analyte signal.



Se Atomic Number 34

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2600 | 0.8 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 1.0 nm |
| Wavelength | 196.0 nm |
| Maximum Absorbance | 1.2 |
| MSR% | 92% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 204.0 | 0.5 |

Performance Data

Characteristic Mass (in argon): 14 µg*

Maximum Ash Temperature: 1200 °C*

Recommended Chemical Modifiers

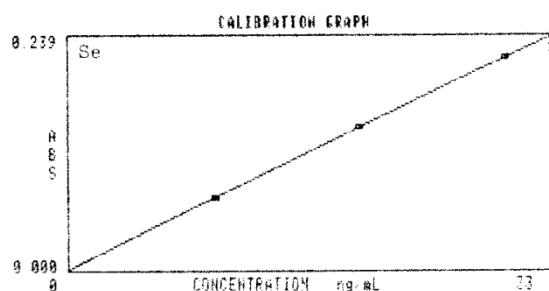
Palladium solution (10 µL of 500 µg/mL)* or

Nickel nitrate solution (50 µg/mL)

Typical Response (Argon): 10 µL of 70 ng/mL gives about 0.2 Abs.*

*Palladium modifier used to obtain these results.

The modifiers permit the use of a higher ashing temperature and enhance the analyte signal.

**Si** Atomic Number 14

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 900 | 5 | 3.0 | Normal | No |
| 5 | 900 | 1 | 3.0 | Normal | No |
| 6 | 900 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 251.6 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 250.7 | 0.5 |
| 252.4 | 0.5 |
| 288.2 | 0.2 |

Performance Data

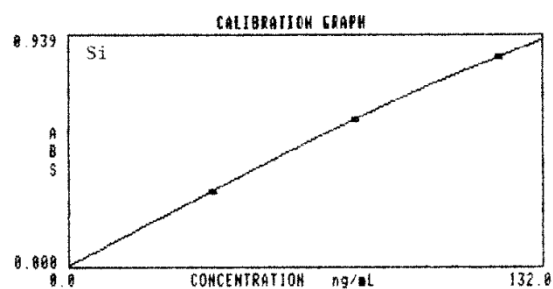
Characteristic Mass (in argon): 15 µg

Maximum Ash Temperature: 1000 °C

Typical Response (Argon): 10 µL of 75 ng/mL gives about 0.2 Abs.

Sodium metasilicate in deionized water was used in obtaining this data.

In the presence of acid, silicon is precipitated from such a silicon standard.



Sn Atomic Number 50

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 700 | 5 | 3.0 | Normal | No |
| 5 | 700 | 1 | 3.0 | Normal | No |
| 6 | 700 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|-----------------------------------|
| Lamp Current | 7 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 286.3 nm, D ₂ 235.5 nm |
| Maximum Absorbance | 1.6 |
| MSR% | 93% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 235.5 | 0.5 |
| 300.9 | 0.5 |
| 266.1 | 0.5 |

Performance Data

Characteristic Mass (in argon): 10 µg*

Maximum Ash Temperature: 800 °C

Recommended Chemical Modifiers

Palladium (5 µL of 100 µg/mL)* or

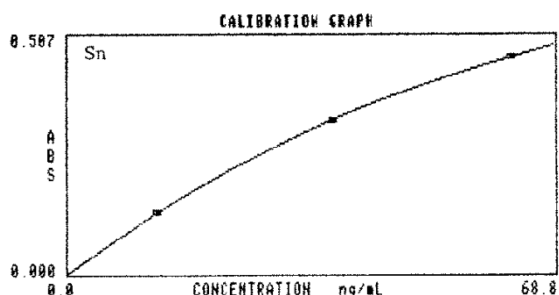
Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 50 ng/mL gives about 0.2 Abs.*

*Palladium modifier used to obtain these results. The use of palladium as the chemical modifier permits the use of a higher ashing temperatures and enhances the signal. The addition of diammonium hydrogen citrate (0.1% solution) to a tin (II) chloride solution also stabilizes the tin in solution and facilitates production of a single atomization peak.

Other complexing agents have also been used, among these are trisodium citrate and EDTA.

Chemical modification of the sample is necessary when analyzing tin in sodium chloride matrices.

**Sr** Atomic Number 38

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 460.7 nm |
| Maximum Absorbance | 2 |
| MSR% | 94% |

Performance Data

Characteristic Mass (in argon): 2 µg

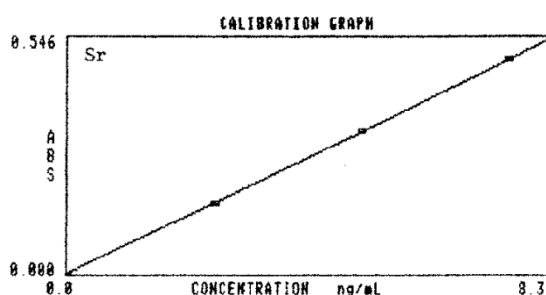
Maximum Ash Temperature: 1100 °C

Typical Response (Argon): 10 µL of 10 ng/mL gives about 0.2 Abs.*

A residual memory may be observed for strontium. This can be eliminated by incorporating a higher temperature tube cleaning step after the atomize stage.

Peak height (rather than peak area) mode should be used for calibration.

At high absorbances, slight upward curvature of the calibration has been observed.



Te Atomic Number 52

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1200 | 5 | 3.0 | Normal | No |
| 5 | 1200 | 1 | 3.0 | Normal | No |
| 6 | 1200 | 2 | 0 | Normal | No |
| 7 | 2600 | 1.1 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 0 | Normal | Yes |
| 9 | 2600 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 214.3 nm |
| Maximum Absorbance | 1.1 |
| MSR% | 93% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 225.9 | 0.5 |
| 238.6 | 0.2 |

Performance Data

Characteristic Mass (in argon): 9 pg*

Maximum Ash Temperature: 1300 °C*

Recommended Chemical Modifiers

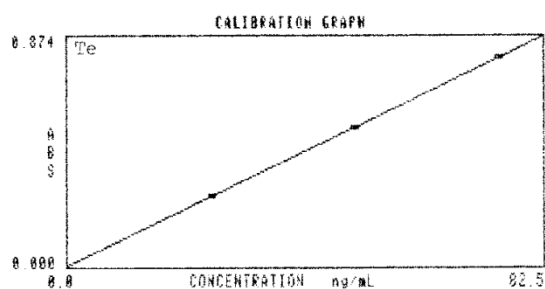
Palladium solution (5 µL of 100 µg/mL)* or

Nickel nitrate 1% solution

Typical Response (Argon): 10 µL of 45 ng/mL gives about 0.2 Abs.*

*Palladium modifier was used to obtain these results.

The modifiers permit the use of a higher ashing temperature and enhance the analyte signal.

**Ti** Atomic Number 22

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1100 | 5 | 3.0 | Normal | No |
| 5 | 1100 | 1 | 3.0 | Normal | No |
| 6 | 1100 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 0.5R nm |
| Wavelength | 364.3 nm |
| Maximum Absorbance | 1.9 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 365.4 | 0.2 |
| 399.0 | 0.5 |

Performance Data

Characteristic Mass (in argon): 50 pg

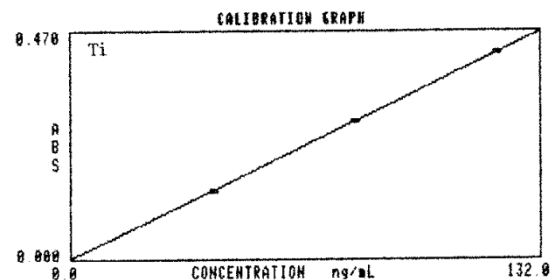
Maximum Ash Temperature: 1400 °C

Typical Response (Argon): 10 µL of 250 ng/mL gives about 0.2 Abs.*

It may be necessary to ensure there is no residual titanium signal before proceeding with an analysis.

A high temperature tube clean step after the atomize stage will help improve precision and accuracy by reducing memory effects.

Measurements should be carried out in the peak height mode, not peak area.



Tl Atomic Number 81

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 250 | 5 | 3.0 | Normal | No |
| 5 | 250 | 1 | 3.0 | Normal | No |
| 6 | 250 | 2 | 0 | Normal | No |
| 7 | 2200 | 1 | 0 | Normal | Yes |
| 8 | 2200 | 2 | 0 | Normal | Yes |
| 9 | 2200 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 276.8 nm |
| Maximum Absorbance | 0.55 |
| MSR% | 63% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 258.0 | 1.0 |

Performance Data

Characteristic Mass (in argon): 15 µg

Maximum Ash Temperature: 400 °C

Recommended Chemical Modifiers

1% sulphuric acid solution or

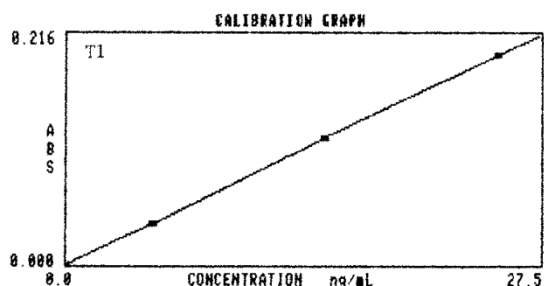
Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Response (Argon): 10 µL of 75 ng/mL gives about 0.2 Abs.

Strong interferences for thallium have been observed in the presence of hydrochloric acid, perchloric acid and sodium chloride. These interferences have been markedly reduced by ensuring that the sample is in 1% sulphuric acid.

Sulphuric acid as a chemical modifier should stabilize the thallium signal.

The palladium chemical modifier permits the use of a higher ashing temperature.

**V** Atomic Number 23

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2700 | 1.3 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 20 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 318.5 nm |
| Maximum Absorbance | 1.8 |
| MSR% | 79% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 318.4 | 0.2 |
| 306.6 | 0.5 |
| 439.0 | 0.5 |

Performance Data

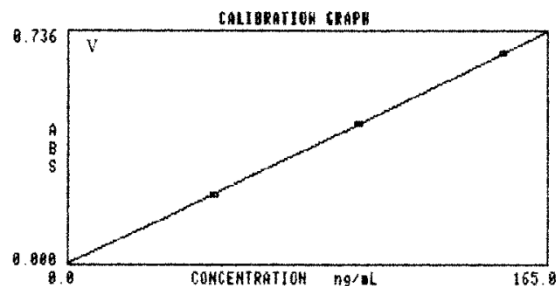
Characteristic Mass (in argon): 22 µg

Maximum Ash Temperature: 1400 °C

Typical Response (Argon): 10 µL of 110 ng/mL gives about 0.2 Abs.

Before attempting any analytical program the following procedure must be carried out

1. Clean the graphite tube (3-5 operations of the Tube Clean).
2. Determine the level of contamination from reagents by measuring a representative blank.
3. Determine any residual levels in the graphite tube after cleaning by operating the furnace program without the addition of samples, standards or blanks.



Yb Atomic Number 70

Matrix 0.1% Hydrochloric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

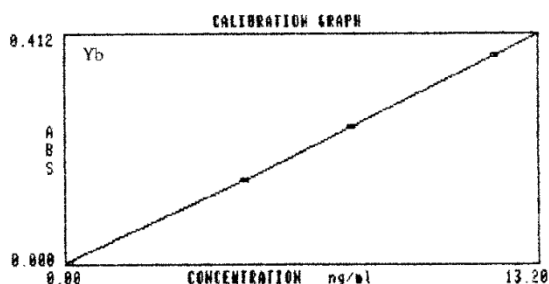
| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 5 | 3.0 | Normal | No |
| 5 | 1000 | 1 | 3.0 | Normal | No |
| 6 | 1000 | 2 | 0 | Normal | No |
| 7 | 2700 | 0.9 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 0 | Normal | Yes |
| 9 | 2700 | 1 | 3.0 | Normal | No |

Instrument Parameters

Lamp Current 5 mA
Spectral Bandwidth 0.5R nm
Wavelength 398.8 nm
Maximum Absorbance 1.0
MSR% 97%

Performance Data

Characteristic Mass (in argon): 3 µg
Maximum Ash Temperature: 1000 °C
Notes: Slight upward curvature has been observed.
Typical Response (Argon): 10 µL of 14 ng/mL gives about 0.2 Abs.



Zn Atomic Number 30

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Coated Partitioned Graphite Tube

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 85 | 5 | 3.0 | Normal | No |
| 2 | 95 | 40 | 3.0 | Normal | No |
| 3 | 120 | 10 | 3.0 | Normal | No |
| 4 | 300 | 5 | 3.0 | Normal | No |
| 5 | 300 | 1 | 3.0 | Normal | No |
| 6 | 300 | 2 | 0 | Normal | No |
| 7 | 1900 | 0.8 | 0 | Normal | Yes |
| 8 | 1900 | 2 | 0 | Normal | Yes |
| 9 | 1900 | 2 | 3.0 | Normal | No |

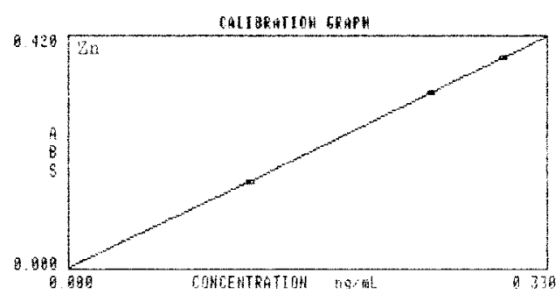
Instrument Parameters

Lamp Current 5 mA
Spectral Bandwidth 1.0 nm
Wavelength 213.9 nm
Maximum Absorbance 0.90
MSR% 92%

| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
|------------------------------|--------------------------|
| 307.6 | 1.0 |

Performance Data

Characteristic Mass (in argon): 15 µg
Maximum Ash Temperature: 400 °C
Typical Response (Argon): 10 µL of 75 ng/mL gives about 0.2 Abs.



Selected Element Data for Pyrolytic Platforms

Al Atomic Number 13

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Platform

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 300 | 30 | 3.0 | Normal | No |
| 2 | 300 | 60 | 3.0 | Normal | No |
| 3 | 1000 | 10 | 3.0 | Normal | No |
| 4 | 1000 | 10 | 3.0 | Normal | No |
| 5 | 1000 | 2 | 0 | Normal | No |
| 6 | 2700 | 1.1 | 0 | Normal | Yes |
| 7 | 2700 | 2 | 0 | Normal | Yes |
| 8 | 2700 | 2 | 3.0 | Normal | No |
| 9 | 40 | 2 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 396.2 nm |
| Maximum Absorbance | 2 |
| MSR% | 100% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 309.3 | 0.5 |
| 237.3 | 0.5 |
| 257.4 | 0.5 |
| 256.8 | 0.5 |

Performance Data

Characteristic Mass (in argon):
Peak Height 2.8 pg
Peak Area 12 pg
Maximum Ash Temperature: 1400 °C
Typical Peak Height Response (Argon): 10 µL of 14 ng/mL gives about 0.2 Abs.
An ash step at 1000 °C may be useful in obtaining a smooth peak shape.
The 309.3 nm line gives an MSR of 88% with a MAX ABS of 0.8 and a slightly poorer sensitivity than at 396.2 nm.

As Atomic Number 33

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Platform

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 300 | 30 | 3.0 | Normal | No |
| 2 | 300 | 60 | 3.0 | Normal | No |
| 3 | 500 | 10 | 3.0 | Normal | No |
| 4 | 500 | 10 | 3.0 | Normal | No |
| 5 | 500 | 2 | 0 | Normal | No |
| 6 | 2600 | 1.1 | 0 | Normal | Yes |
| 7 | 2600 | 2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 3.0 | Normal | No |
| 9 | 40 | 11.8 | 3.0 | Normal | No |

Instrument Parameters

| | |
|------------------------------|--------------------------|
| Lamp Current | 10 mA |
| Spectral Bandwidth | 0.2 nm |
| Wavelength | 193.7 nm |
| Maximum Absorbance | 0.95 |
| MSR% | 86% |
| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
| 197.2 | 1.0 |

Performance Data

Characteristic Mass (in argon):
Peak Height 15 pg*
Peak Area 46 pg*
Maximum Ash Temperature: 1500 °C*
Recommended Chemical Modifiers
Palladium (10 µL of 500 µg/L) or
Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368)
or
Nickel solution (50 µg/mL)
Typical Peak Height Response (Argon): 10 µL of 114 ng/mL gives about 0.2 Abs.
*Palladium modifier used to obtain these results.

Hg **Atomic Number 80**

Matrix 1.0% Nitric Acid
Atomizer Pyrolytic Platform

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 300 | 30 | 3.0 | Normal | No |
| 2 | 300 | 60 | 3.0 | Normal | No |
| 3 | 500 | 10 | 3.0 | Normal | No |
| 4 | 500 | 10 | 3.0 | Normal | No |
| 5 | 500 | 2 | 0 | Normal | No |
| 6 | 2600 | 1.1 | 0 | Normal | Yes |
| 7 | 2600 | 2 | 0 | Normal | Yes |
| 8 | 2600 | 2 | 3.0 | Normal | No |
| 9 | 40 | 12.8 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 4 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 253.7 nm |
| Maximum Absorbance | 0.35 |
| MSR% | 69% |

Performance Data

Characteristic Mass (in argon):

Peak Height 150 pg*

Peak Area 250 pg*

Maximum Ash Temperature: 500 °C*

Recommended Chemical Modifiers

Pd solution (1000 µg/mL)* or

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368) or

Diammonium sulphide in excess.

Typical Peak Height Response (Argon): 10 µL of

505 ng/mL gives about 0.2 Abs.

*Pd modifier used to obtain these results.

The palladium modifier is pre-injected, and taken to step 3.

The palladium modifier permits the use of a higher ashing temperature and enhances the signal.

The diammonium sulphide modifier stabilizes the mercury signal.

Fresh dilutions of mercury standards should be prepared each day as the standards are not very stable.

Pb **Atomic Number 82**

Matrix 0.1% Nitric Acid
Atomizer Pyrolytic Platform

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 300 | 30 | 3.0 | Normal | No |
| 2 | 300 | 60 | 3.0 | Normal | No |
| 3 | 500 | 10 | 3.0 | Normal | No |
| 4 | 500 | 10 | 3.0 | Normal | No |
| 5 | 500 | 2 | 0 | Normal | No |
| 6 | 2400 | 1 | 0 | Normal | Yes |
| 7 | 2400 | 2 | 0 | Normal | Yes |
| 8 | 2400 | 2 | 3.0 | Normal | No |
| 9 | 40 | 11.8 | 3.0 | Normal | No |

Instrument Parameters

| | |
|--------------------|----------|
| Lamp Current | 5 mA |
| Spectral Bandwidth | 0.5 nm |
| Wavelength | 283.3 nm |
| Maximum Absorbance | 1.4 |
| MSR% | 92% |

| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
|------------------------------|--------------------------|
| 217.0 | 1.0 |
| 261.4 | 0.5 |

Performance Data

Characteristic Mass (in argon):

Peak Height 5 pg*

Peak Area 15 pg*

Maximum Ash Temperature: 600 °C*

Recommended Chemical Modifiers

Ammonium dihydrogen orthophosphate (5 mg/mL)* or

Orthophosphoric acid (1000 µg/mL) or

EDTA, citrate, oxalate (0.5 – 1% v/v) – See Chapter One or Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Peak Height Response (Argon): 10 µL of 25 ng/mL gives about 0.2 Abs.

*Ammonium phosphate modifier used to obtain these results.

Phosphate chemical modifiers permit the use of a higher ashing temperature and stabilize the lead signal.

The use of EDTA, citrate or oxalate stabilizes the lead allowing it to atomize at a lower temperature than does a nitrate or chloride matrix. The palladium chemical modifier permits the use of a higher ashing temperature.

Lead is a common contaminant in reagents and it is essential that a representative blank is measured before proceeding with the analytical program.

The atomization temperature can be altered by chemical modifiers. The chemical matrix plays an important role in determining optimum ash and atomizing conditions. It is strongly recommended that the ash steps be extensively investigated.

Non-atomic absorption may be higher at the 217.0 nm line, for which the MAX ABS is 0.6 and the MSR is 71%.

Sn Atomic Number 50

Matrix 0.1% Nitric Acid

Atomizer Pyrolytic Platform

Furnace Operating Conditions

| Step No. | Temp. (°C) | Time (sec) | Gas Flow (L/min) | Gas Type | Read Command |
|----------|------------|------------|------------------|----------|--------------|
| 1 | 300 | 30 | 3.0 | Normal | No |
| 2 | 300 | 60 | 3.0 | Normal | No |
| 3 | 500 | 10 | 3.0 | Normal | No |
| 4 | 500 | 10 | 3.0 | Normal | No |
| 5 | 500 | 2 | 0 | Normal | No |
| 6 | 2900 | 1.2 | 0 | Normal | Yes |
| 7 | 2900 | 1.0 | 0 | Normal | Yes |
| 8 | 2900 | 1.0 | 3.0 | Normal | No |
| 9 | 40 | 14.3 | 3.0 | Normal | No |

Instrument Parameters

Lamp Current 7 mA

Spectral Bandwidth 0.5 nm

Wavelength 286.3 nm

Maximum Absorbance 1.6

MSR% 93%

| Alternative Wavelengths (nm) | Spectral Bandwidths (nm) |
|------------------------------|--------------------------|
| 235.5 | 0.5 |
| 300.9 | 0.5 |
| 266.1 | 0.5 |

Performance Data

Characteristic Mass (in argon):

Peak Height 12 pg*

Peak Area 60 pg*

Maximum Ash Temperature: 800 °C*

Recommended Chemical Modifiers

Palladium solution (5 µL of 100 µg/mL)* or

Palladium solution (500-2000 µg/mL) plus reducing agent such as ascorbic acid (368).

Typical Peak Height Response (Argon): 10 µL of 60 ng/mL gives about 0.2 Abs.*

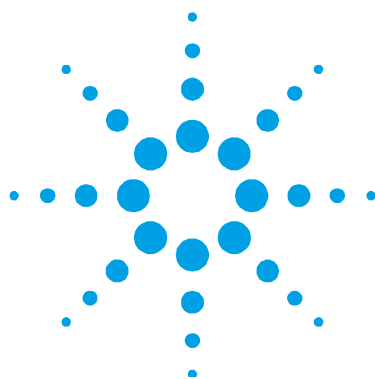
* Palladium modifier used to obtain these results. The use of palladium as the chemical modifier permits the use of higher ashing temperatures and enhances the signal.

The addition of diammonium hydrogen citrate (0.1% solution) to a tin (II) chloride solution also stabilizes the tin in solution and facilitates production of a single atomization peak.

Other complexing agents have also been used, among these are trisodium citrate and EDTA.

Chemical modification of the sample is necessary when analyzing tin in sodium chloride matrices.

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5. Standard and Sample Preparation

Analysts must recognize that the graphite furnace technique demands a particularly high standard of care in all activities which affect the accuracy and precision of the analytical result. Scrupulous cleanliness is essential in all laboratory procedures. Standards and samples must be meticulously prepared and carefully handled. Ideally, the laboratory should be air-conditioned and dust free, preferably draught free as well. Unless the laboratory has been correctly prepared, satisfactory results may never be obtained with microanalytical techniques using graphite tube atomizers.

Strict precautions must be taken to avoid contamination of apparatus, and even though laboratory ware is stored under ideal conditions, it should be thoroughly rewashed before use (see 'Apparatus' below). Strict care should also be taken to avoid contamination of all reagents and distilled water. Ideally, reagents should be entirely free of the element of interest, but this is obviously impossible for all analyte elements in all reagents (see also 'Blank Solutions', 'Water', 'Reagents').

Apparatus

All laboratory apparatus should be scrupulously clean. This includes all beakers, watchglasses, pipettes and volumetric flasks (54-61). Even when clean glassware has been stored under ideal conditions it should be thoroughly rewashed before use. Use the following procedures for cleaning glass and plastic apparatus.

Fill the vessel with 20% v/v hydrochloric acid and leave for about 2 days, Include the plastic lid in the leaching and cleaning process. Discard the acid solution, and fill the vessel with 20% v/v nitric acid and leave for a further 2 days. Again, include the plastic lid in this leaching and cleaning process. Discard the nitric acid, and rinse the vessel thoroughly with distilled water. The vessel can then be filled with distilled water and left until required, or it can be thoroughly air dried, Always ensure that air-borne particles cannot fall into the vessel prior to use.

Blank Solutions

A blank solution is defined as a solution containing all the reagents to be added to the sample but excluding the sample itself. Contamination of the water and reagents used in the preparation of standards and samples can cause a high blank signal in furnace atomization.

Always check for contamination in the blank solution. A consistent blank reading must be obtained before analytical data is taken.

Water

Water is the most commonly used reagent for both sample dissolution and dilution, therefore steps must be taken to ensure it is contamination free. Distilled water is usually contaminated with dissolved gases or organic material. Many investigators (54, 55) have found that when metallic or pyrex vessels are used in the distillation of water, the water produced generally contains a high level of cationic impurities. A cation-exchange resin must be used as well as distillation techniques to remove these impurities.

The American Society for Testing and Materials (ASTM) (56,57) has graded various types of reagent water. Combinations of ion-exchange, reverse osmosis, distillation, filtering or electrodialysis techniques are used to produce each type of water. Type 1 is suitable for trace analysis and is defined as water prepared by the distillation of feed water having a maximum conductivity of 20 $\mu\text{mho/cm}$ at 25 °C followed by polishing with a muted bed of ion-exchange materials and a 0.2 μm membrane filter.

Ideally any hard waters should be pretreated by a water softening process to remove any calcium and magnesium that may form scale in the distillation unit, then passed over a carbon filtration system to remove any organics. After slow distillation the water should be slowly passed through an ion-exchange column in which one stage is a strongly acidic cation-exchange resin in the hydroxyl form.

Some of the commercially available purification systems that can be used for the production of high purity water are the Millipore Super-Q System (58,62) and a system produced by the Continental Water Conditioning Corporation. The Millipore system consists of disposable cartridges for each purification step. Frequent monitoring to ensure optimum performance is required no matter which system is chosen. A conductivity meter placed between the still and the storage vessel will indicate whether or not the system is working at maximum effectiveness.

Reagents

Always use the purest grade reagents available for all trace analyses. Reagent manufacturers usually indicate the contaminants and specify the levels. Use these as a guide but always check the levels prior to the analysis. Even the highest grade available will not be pure enough for particularly stringent analyses, and further purification will be necessary.

Edwin C. Kuehner et al (63) have developed procedures for purifying mineral acids including hydrofluoric acid. A quartz sub-boiling still was used for the production of HCl, HNO_3 , HClO_4 , H_2SO_4 and H_2O . Infra-red radiators heat the liquid being distilled, evaporating it without boiling. The condenser is angled so that the distillate can drip to the outlet more efficiently. A liquid level control maintains the liquid to just below the overflow height, therefore ensuring a constant volume of 400-500 mL of liquid in the still.

Hydrofluoric acid is led through a PTFE sub-boiling still. The PTFE still operates in a very similar manner but modifications were made to allow for the different surface tension of the PTFE. The operating temperature is also restricted by the softening properties of PTFE.

Other reagents used must also be checked for impurities and purified if necessary (64). This could involve recrystallization if the reagent is a solid or sublimation if the reagent is a liquid.

The vacuum sublimation behavior of various metal chelates has been studied by Honjo et al (65). Many reagents can be purified using this technique.

Even after reagents have been purified it is still essential to prepare blank solutions for each analysis. This is to ensure that the results obtained for the analysis are in no way affected by residual contamination.

Standard Preparation

Two sources of standards are available to the analyst.

- Commercially prepared standards usually with a concentration of 1000 $\mu\text{g/mL}$ of the element of interest.
- Standards prepared in the laboratory by the analyst from the pure metal or pure metallic salts.

Either is suitable for furnace techniques. These standards are usually stable for many months, especially when a stabilizer has been included in the initial preparation. For most elements the stabilizer is a mineral acid, usually hydrochloric or nitric acid.

Fresh working standards should be prepared daily to avoid either a loss of analyte on the container wall or conversely, leaching out of the element from the container. It is good practice to perform serial dilutions rather than make one large dilution. For example, to perform a dilution of 1 in 10,000, make two separate dilutions: 1 in 100 and then a further 1 in 100. The errors in the latter procedure will be much smaller than dilutions of, for example, 0.1 mL in 1 L to make a 1 in 10,000 dilution. To further decrease these errors use only grade A glassware.

Check the volume delivered by weighing an aliquot of water. If, for example, a 10 mL volumetric pipette is being used, the mass delivered should be 10.0 g (since the density of water is equivalent to unity). If the mass delivered is incorrect, then appropriate volumetric corrections will be needed. (Ambient temperature must be taken into account in this calculation.) By taking these precautions the error involved in the dilution steps should be minimized. For information about calibration and selection of standards, refer to 'Calibration Procedures' later in this chapter.

Sample Preparation

Each type of sample to be analyzed by graphite furnace AA requires a specific preparation according to its matrix. Digestion procedures for specific types of samples are given in Chapter Seven.

It is normally essential to have a sample solution which is homogeneous. If the solution is not homogeneous (it may contain suspended particulates for example), a representative sample may not be dispensed into the graphite tube atomizer. This will lead to inaccuracies in the analysis.

It is generally necessary to study the behavior of your samples in the graphite tube atomizer to establish the optimum operating parameters. Proceed as follows:

Optimize the system for maximum light transmittance or minimum absorbance initially by following the procedure outlined in the Operation Manual.

It is important that the standards should be prepared such that their behavior in the graphite tube atomizer is similar to that of the samples.

Using a representative standard, optimize the heating program of the graphite tube atomizer, being guided by the analytical data in Chapter Four. Always perform two or three blank firings of the furnace to ensure a constant blank level. A reagent blank should also be determined to check for any contamination.

Examine Figure 20 which shows how the appropriate sample volume can be selected to achieve an absorbance signal in the correct absorbance range for best precision. Dilution may be necessary if the analyte concentration is too high. Concentration techniques may be necessary if the concentration is too low.

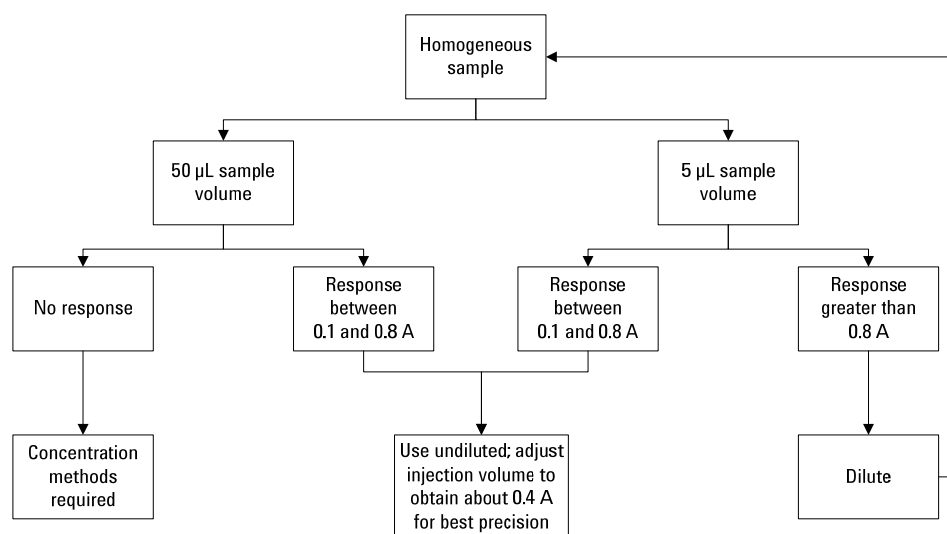


Figure 20. Scheme for selection of correct sample dilution for analysis by GTA

Generally the sample need not be diluted any further than one hundred times. If it is found that the sample is still too concentrated then flame AA should be considered since the levels in the original sample would normally be within the working range for flame analysis. Often, when the available sample volume is too small for flame AA, then further dilutions will be necessary for analysis by graphite tube atomizer. Flame microsampling methods are an alternative technique for analyzing the sample. Using this method a small volume of sample (typically 50 or 100 μL) is injected into a specially designed PTFE cup and atomized in the flame.

After determining the approximate analyte concentration, the sample can then be categorized accordingly. The categories are discussed under the heading 'Calibration Procedures'.

Storage

Samples

Samples should be analyzed as soon as possible after collection and preparation. This will minimize any errors due to contamination from the container or loss of analyte on to the container walls. Avoid using glassware to store samples since some metals may be adsorbed on to the glass surface. It is best to transfer the sample to polyethylene containers as soon as the dissolution procedure has been completed.

To minimize any contamination or loss of analyte:

- Clean containers carefully (as previously described).
- Analyze the samples on the same day as they are prepared
- Where possible, acidify the sample to about pH 2 or less.

Standards

Always ensure that the containers used for storage have been thoroughly cleaned using the procedures previously described. As a general rule standards having a concentration of 1000 $\mu\text{g}/\text{mL}$ are stable for months when acidified to a pH of 2 or less. These can be stored in polyethylene bottles, tightly capped. Always make up fresh standards for each analysis to ensure accuracy. Usually when the analyte concentration is less than 1 $\mu\text{g}/\text{mL}$ the solution will only last for a few days. This will depend on the element and the standard matrix. Where possible, acidify with a mineral acid to pH 2 or less.

Note that acid must not be added to cyanide standards. Photographic waste products often contain cyanide complexes, and acids should not be added to stabilize the standards.

Remember:

- Standards should be prepared immediately prior to the analysis.
- The analyst should be aware of the standard matrix before adding any chemical designed to enhance the stability of the element in solution.
- Containers must be meticulously cleaned.

Interferences

Many interference effects have been described, but they can generally be categorized as physical or chemical in the mechanism by which they are produced.

Physical Interferences

Viscosity and Surface Tension

Furnace determinations can be physically affected by differences in viscosity and surface tension between standards and samples. Such physical interferences in simple analytical situations may be minor and analytically insignificant. In more complicated situations they may be relatively severe, and small variations in physical properties can have a large influence on the final result. This can only be countered by close physical matching of standards and samples.

These interferences may occur in two ways:

First, the more viscous solutions (oils and some biological materials for example) tend to cling to the pipette and a significant proportion will not reach the furnace. More mobile solutions, on the other hand, may creep over the outside of the pipette, and again a significant proportion will not reach the furnace. Some solutions at high acid concentrations (20% to 50%), and some organic solvents, are examples of this behavior.

Second, the extent to which solutions spread over the inside surface of the furnace is a function of viscosity and wetting characteristics. Differences in spreading can significantly affect the absorption signal because the residence time of atoms within the observation zone will vary depending on how far from the center the atomization occurs.

Background Absorption

In furnace analyses, background absorption can be significant at wavelengths up to about 340 nm, and the background signal may exceed 1.0 Absorbance. There are three counter-measures available to the analyst - background correction, appropriate temperature programming, and chemical modification.

Background correction should always be used when first developing a furnace method. First, to obtain a valid analytical result. Second, to find out whether background absorption is occurring or not and measure the actual background signal if necessary. Third, to monitor the effectiveness of the other counter-measures.

It is preferable to exploit temperature programming, chemical modification, or both, rather than relying solely on background correction.

In the background absorption context, the objective of temperature programming is to either:

- Ensure that matrix material which causes background absorption is removed prior to the atomization stage without loss of analyte,

or

- Create a time lapse between the background signal and the analyte signal such that the two signals are separately observed and measured.

Chemical Interferences

These interferences originate from the formation of compounds which are either excessively volatile or excessively stable within the furnace environment.

In those compounds which are excessively volatile, the analyte is lost at low temperatures during drying or ashing without undergoing atomization. If, for example, the analyte will readily form a covalent chloride, the presence of excess chloride ions may cause the analyte to appear as a volatile chloride which will vaporize before it can be decomposed to the atomic form. The loss of analyte in this way will obviously degrade analytical sensitivity, and care may be needed with elements which form volatile halides. Particular attention to the original solution chemistry can often avoid or minimize the effect. Alternatively, it may be necessary to use a chemical modifier.

Interferences can be encountered when the analyte forms two or more stable compounds which finally dissociate at different temperatures. In this situation, analyte is not lost during drying or ashing. But, the atomic concentration of interest becomes associated with two or more compounds, and the atomic signal is dissipated amongst multiple atomization peaks instead of appearing as a single coherent response. For some samples it is possible to avoid or minimize the interference by revising the original solution chemistry. For other samples a chemical modifier may be needed to isolate the analyte in a specific form and prevent the formation of interfering compounds.

An extreme case of excessive stability occurs when the element forms a refractory carbide. This may degrade the analytical sensitivity; give a significant memory effect, or both. Elements such as barium, molybdenum, titanium and vanadium will readily form such carbides. They can, however, be successfully determined in pyrolytically coated graphite furnaces since the pyrolytic coating reduces the tendency to form carbides. Other elements such as tantalum, tungsten and zirconium are quite difficult to determine, largely because of the readiness with which they form refractory carbides even in a pyrolytic environment.

Calibration Procedures

Before deciding whether to use standard additions calibration or normal concentration calibration, the analyst needs as much information as possible about the sample composition. The type of calibration procedure to be used will depend on the complexity and nature of the sample. This is more fully discussed later in this chapter under the following headings:

- Simple Aqueous Matrices
- Complex Known Aqueous Matrices
- Complex Unknown Aqueous Matrices
- Organic Matrices

The preferred absorbance range is about 0.1 to 0.8 but this will of course depend on the maximum absorbance. The sample absorbances should always lie within the absorbance range of the standards. Determine each standard calibration point in triplicate to establish its validity. When using a previously compiled method, check the calibration graph displayed on the screen (if necessary produce a printed copy) before proceeding with the analysis. If the calibration linearity and working range are satisfactory, the analysis may proceed. Otherwise, make whatever changes to the standards that the situation requires and re-check the calibration before proceeding further.

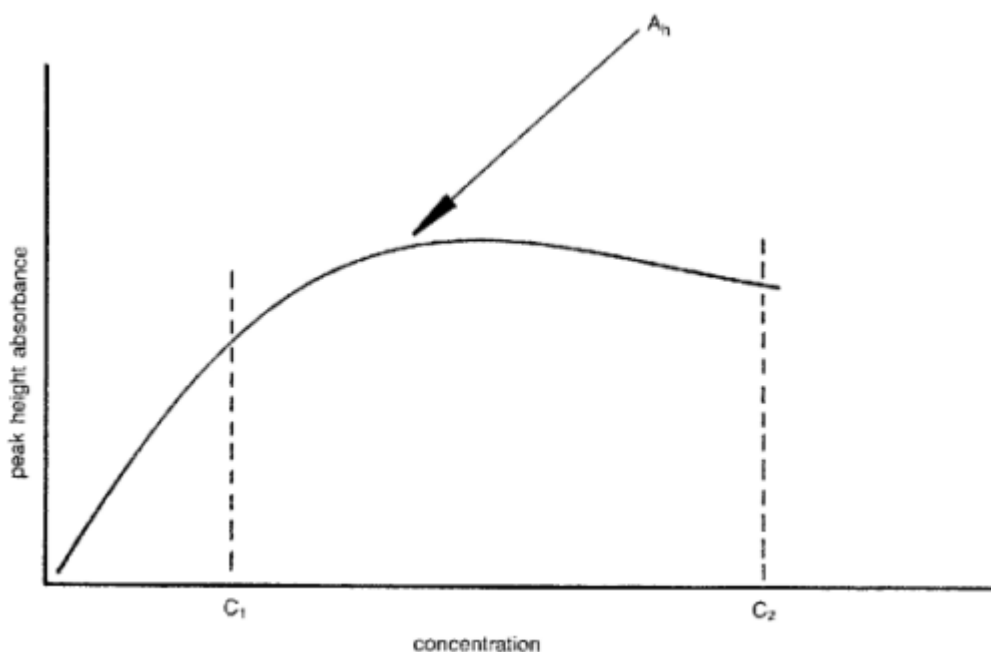


Figure 21. Calibration using Zeeman absorbances

Establishing a New Calibration

At the appropriate stage of method development you should always produce a calibration graph so that the maximum absorbance, calibration linearity and working range can be properly assessed. Refer to Figure 21 and note the following criteria when initially establishing the calibration using Zeeman absorbances:

- 1 Use PEAK HEIGHT measurements.
- 2 The calibration graph over the working concentration range 0 to C_1 should be substantially linear.

- 3 ALWAYS investigate the calibration graph up to a concentration which is high enough to observe roll-over or the limiting absorbance (this will be concentration C_2 in Figure 21). As a general rule, this will require extension to a concentration which is between 5 and 10 times concentration C_1 or a concentration at least 5 times the concentration at the highest absorbance A_h .
- 4 Calculate the MAX ABS as follows:
 - a From the calibration graph, establish a value for the highest absorbance A_h .
 - b As a general rule, MAX ABS can be taken as $A_h \times 0.8$.
- 5 Use the numerical keyboard and enter the value for MAX ABS as described in the spectrometer Operation Manual.
- 6 As shown in Figure 21, and as explained in Chapter Two, the same absorbance can be given by two different concentrations. By establishing a suitable value for MAX ABS and entering this value as part of the method, the instrument will automatically produce an error message if this value is exceeded. This will avoid the possibility of obtaining the same absorbance measurement at two different concentrations. Remember, however, that you MUST NOT attempt to perform practical analyses beyond the upper working limit defined by the MAX ABS.
- 7 The MAX ABS value will always be higher than the absorbance for concentration C_1 but you should not assume that the working range can be arbitrarily extended up to MAX ABS. Remember that it is analytically preferable to operate on that portion of the calibration graph which is substantially linear.

Calibration Check

It is good analytical practice to check the calibration at particular intervals during your analytical program. Frequency of calibration will depend on the accuracy and precision required, and the type of samples being analyzed. Guidance regarding the optimum frequency of calibration is usually given in the methodology. Use the RESLOPE facility where this is analytically valid. Otherwise, re-calibrate against all standards. For IVO analyses, work strictly in accordance with all instructions given in the methodology.

Standards

For standard additions methods, refer to the guidelines given under 'Complex Unknown Aqueous Matrices'. For normal concentration calibration the following guidelines may be helpful in selecting standards:

- Only one standard is needed when the working range is strictly within the linear portion of the calibration graph.

Note that there is one special case where a single standard is almost always adequate. This is when working at an absorbance of 0.1 or lower, but where the sample concentration is at least ten times the detection limit.

- If the working curve is non-linear, but the deviation from linearity is small, two or three standards should be used. Four or five standards can be used when the working curve is nonlinear, or where the maximum working range is required. Note, however, that analysis time will be extended, and analytical accuracy may not always be improved.

When using multiple standards, the lowest standard must be within the linear portion of the calibration graph. As a general rule, your lowest standard should be selected to give an absorbance of about 0.1.

- There is a special case for the use of two standards. This is the 'bracketing standards' method in which the concentrations of the standards are slightly lower and higher than the expected sample concentration.
- Remember that some solution schemes may be such that standards and samples do not contain identical volumes of blank or identical volumes of chemical modifier. In these circumstances, the contribution from blank or modifier to the analytical signal will not be the same for all solutions. The difference must be established and allowed for.

Simple Aqueous Matrices

It is usually sufficient to prepare a series of aqueous standard solutions - nitric acid standards for nitric acid digested samples, for example. Peak height or peak area measurements may be used although for some high temperature elements it is preferable to use peak height measurements (refer to Chapter Three). The calibration will be automatically computed and displayed on the video screen.

Multiple injection procedures can be performed manually to enhance the analyte signal when using the hand-injected technique, or they can be performed automatically (see also Chapter Six).

A few points to remember are:

- Method development will be required for each type of sample - refer to Chapters Three and Four.
- For manual operation, the multiple injections must be carried out at the appropriate point in the program, and suitable time periods must be built into the program to provide time for the injections. This period will vary according to analytical circumstances and the dexterity of the operator (it may need to be determined experimentally).
- When multiple injections are being placed manually in the graphite tube, any errors are additive. Careful placement of the droplet will aid precision, but analysts should remember that an additional error is likely to occur with each injection.
- As described in Chapter Three, a step is required to allow the gas flow to stop prior to the atomization stage.

Complex Known Aqueous Matrices

When samples such as steels, ores and other defined samples are to be analyzed, interferences between elements can occur. In a quality control situation, where the matrices are known, the standards can be chemically matched with the samples so that the behavior of standards and samples will be similar. For example, when steel is being analyzed for its aluminum content, the standards should include constituents such as nickel, chromium, copper and iron at approximately the same concentrations as the sample.

Even for some complex samples, it is sometimes possible to use simple aqueous standards. Generally, the steps prior to atomizing the sample will completely remove the remainder of the sample matrix. Complexing reagents can be used for this purpose (see Chapter Seven), but each sample must be considered on its own merits.

Complex Unknown Aqueous Matrices

With complex samples, it is unlikely that the chemical and physical properties of standards prepared by normal methods will match those of the sample. Consequently, the behavior of sample and standards during drying, ashing and atomization will not be identical, and analytical errors may occur. In these circumstances the standard additions technique should be used.

With the standard additions technique, mismatch between samples and standards is minimized because the standards are prepared from the actual samples. The general procedure is to take several aliquots of sample, add different quantities of analyte element to each aliquot and dilute to the final volume. These solutions then form a series of standards of different concentration. One aliquot is used without the addition of analyte element.

The quantities of analyte added are based on the expected concentration in the sample. If, for example, you use three standards, typical additions would be 50%, 100% and 150% of the concentration predicted in the sample.

Table 4 Typical standard additions dilution scheme*

| Solutions | mL Sample | mL Standard (0.1 µg/mL) | mL Solvent | Final Volume (mL) |
|-----------|-----------|----------------------------|------------|-------------------|
| No. 1 | 5.0 | — | 5.0 | 10 |
| No. 2 | 5.0 | 1.0 | 4.0 | 10 |
| No. 3 | 5.0 | 2.0 | 3.0 | 10 |
| No. 4 | 5.0 | 3.0 | 2.0 | 10 |

Table 5 Concentration of Analyte

| Solutions | Concentrations Present in Solutions Prepared |
|-----------|--|
| No. 1 | Original sample concentration (µg/mL) x 1/2 |
| No. 2 | Elemental concentration (µg/mL) x 1/2 + 0.01 (µg/mL) |
| No. 3 | Elemental concentration (µg/mL) x 1/2 + 0.02 (µg/mL) |
| No. 4 | Elemental concentration (µg/mL) x 1/2 + 0.03 (µg/mL) |

*Expected elemental concentration about 0.02 µg/mL.

By constructing a linear plot as shown in Figure 22 and extrapolating to zero absorbance, the concentration of the sample can be calculated.

When a sample type is being analyzed for the first time it is good analytical practice to compare the standard additions method with the normal calibration procedure. If the gradients of the two plots are equivalent, it can be assumed that there is negligible chemical interference and the standard additions technique would be unnecessary. Figure 22 illustrates an analytical situation where the standard additions curve and the calibration curve are parallel. This indicates that the standard additions method is not required.

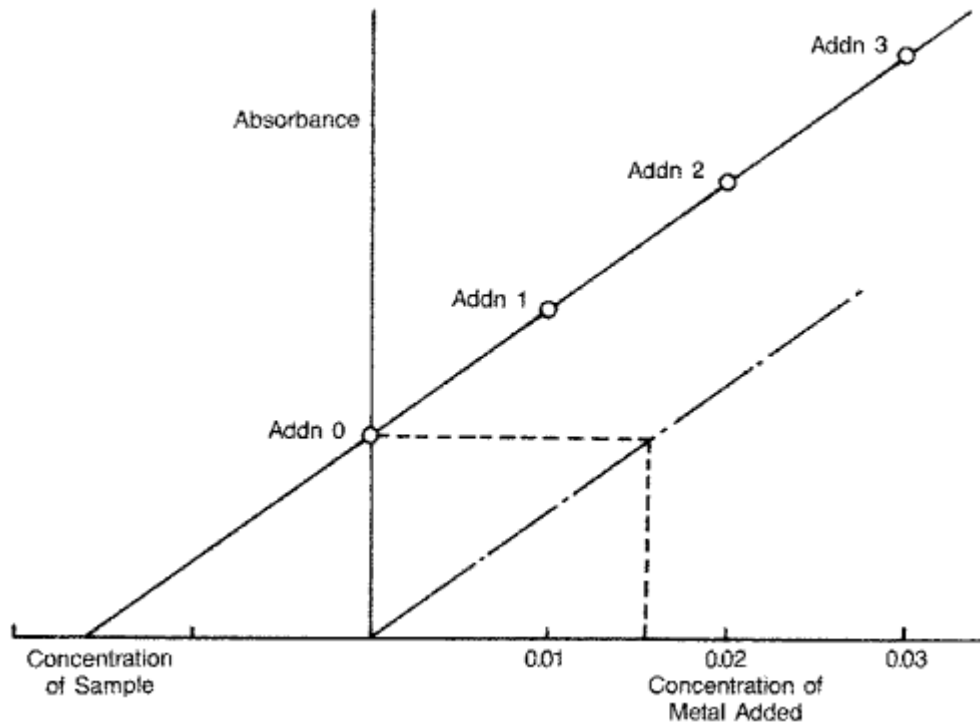


Figure 22. Standard additions graph

Prepare the appropriate addition standards in accordance with the following criteria:

- The standards MUST be within the linear portion of the calibration graph. The automatic calibration program is based on linear regression and an accurate result cannot be calculated from non-linear calibration points.
- You may use up to five standards plus the zero addition.
- You will also need a reagent blank to establish the baseline.

In the most rigorous application of this technique, each individual sample must be analyzed separately against a set of addition standards which are specific for that sample. Under some circumstances, however, it is possible to analyze a number of samples against a single set of addition standards. This method can, of course, only be used where the samples are chemically and physically similar. The similarity must be such that the regression calibration established from the single set of addition standards is valid for all of the samples in the program.

The SpectrAA system enables you to use either of these methods automatically. In addition, the system can be programmed to use either addition standards prepared in your laboratory (SAMPLER PREMIXED), or, addition standards prepared automatically by the sample dispenser (SAMPLER AUTOMIXING).

Sampler Premixed

This is explained more fully in Chapter Six. Complete operational details are given in the Operation Manual.

This mode is intended to be used where it is preferable to prepare the addition standards in the laboratory.

The complete carousel load must consist of a series of batches, each batch containing blank, addition standards and sample (addition 0). All batches must have the same number of standards.

You may include more than one sample in each batch if this is analytically valid. In this circumstance, each batch must include the same number of samples as well as the same number of standards.

If you are proposing to use a modifier solution, you do not need to include the modifier when preparing your addition standards in the laboratory. The sample dispenser can be programmed to add the required volume of modifier solution.

The analytical program can be performed completely automatically, or semi-automatically.

Sampler Automixing

This is explained more fully in Chapter Six. Complete operational details are given in the Operation Manual.

This mode is intended to be used where it is preferable to have the addition standards prepared automatically by the sample dispenser.

The addition standards will be prepared in accordance with the solution scheme that you compile on the SAMPLER page.

The analytical program can be performed completely automatically, or semi-automatically.

Organic Matrices

To establish an accurate calibration it is necessary to use organic standards (56). Organometallic standards are now commercially available in two forms:

- Oil-soluble organometallic powders
- Organometallic compounds in oil.

Suppliers of these standards include Conostan, B.D.H Chemicals and National Spectrographic Laboratories Inc. (57-69). The appropriate range of standards can be prepared by diluting with the required solvent.

It is important to ensure that samples and standards have closely similar viscosities. For example, ensure that the required amount of blank oil is added to the standards. Always quote the method used to prepare the standards, that is, weight per volume, volume per volume or weight per weight. Conversion is possible if the specific gravity of the diluting solvent is known (70, 71).

The rules applicable to aqueous standards are equally applicable to organic standards. A reagent blank must be prepared and corrected for in all analyses. Once the blank level has been established the absorbance working range should be from 0.1 to 0.8 to obtain the best precision.

When standards are to be stored for any length of time, a stabilizer should be added to maintain the correct concentration levels.

Organic solvents that can be used for furnace analysis include 4-methyl-pentan-2-one (MIBK), xylene and kerosene. Tetrahydrofuran (THF) can also be used for furnace analysis. This has the further advantage of being miscible in both water and oils. When using organics over a prolonged period, ensure that the containers are well sealed since evaporation will occur, and thus increase the relative elemental concentration.

As with aqueous solutions, containers must be thoroughly cleaned and dried completely before use with organic solvents.

Manual Injection Techniques

Each operator will develop an individual style when introducing a sample into the graphite tube atomizer, but the following general rules should be observed:

Ensure that the sample is completely in the tube. A poor injection may leave some sample smeared across the injection hole which will lead to low results and poor precision.

After a determination, the graphite tube atomizer will cool to ambient temperature. The temperature scale shown on the VDU screen indicates the temperature of the graphite tube. A message prompting the operator to inject the next sample will be automatically displayed on the video screen.

Always use both hands to inject the sample. One hand should be used to support and steady the hand holding the pipette. For consistent injections keep the pipette vertical and observe the position of the hole in the carbon furnace. Very lightly touch the bottom surface of the graphite tube, then lift slightly and inject. Injection is accomplished by an even, steady depression of the plunger through the first stop and, on some brands of dispensers, to the second stop.

Withdraw the pipette carefully, holding the plunger down. Low and inconsistent results can occur if the plunger is released since some of the sample can be pulled back into the tip.

Figure 23 shows the steps required for consistent sample injection,

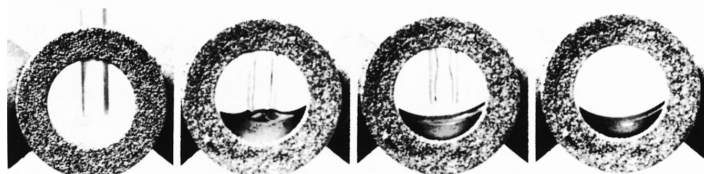


Figure 23. Manual injection of sample into graphite tube atomizer

Once the operator has become competent at injecting samples, precision of about $\pm 5\%$ can be expected for a dilute acid or aqueous matrix. The precision obtainable from the graphite tube is dependent upon the type of sample matrix and the element being monitored. Much better precisions can be achieved with some elements and solutions, especially when the autosampling accessory is operating. The micropipette has an inherent precision of approximately $\pm 1\%$.

Syringes and Their Maintenance

Observe the manufacturer's recommendations for maintenance. These instructions usually explain the correct cleaning and maintenance procedure. To maintain a reproducible sampling volume, avoid contacting the sample with the dispenser or the needle. If the two are brought into contact, cleaning will be necessary because subsequent samples will be contaminated or the mechanical parts of the syringe will be corroded. Syringes should be cleaned regularly. If they are dismantled, ensure that the components are reassembled in the correct manner.

Pipette tips are another potential source of contamination; most are of the disposable type and may require cleaning prior to use. The most effective method for cleaning is to soak the batch of tips overnight in a dilute nitric acid solution. Rinse the tips repeatedly with distilled water, dry in a vacuum desiccator and store in a cleaned, contamination-free container. The most commonly found contaminants in plastic pipette tips include zinc, magnesium and sodium.

Do not touch the tips while attaching them to the syringe as this is a sure way of introducing contamination. During the analysis a new tip should be used for each standard or sample. If for any reason the same tip must be used more than once, ensure that it is thoroughly flushed out to avoid cross-contamination. After initiating the operating program, place the syringe in a position where the tip cannot become contaminated.

System Errors

Several problems which can affect precision and accuracy may be encountered at different stages of the analysis. These contribute to the total response and are dependent upon the matrix, element and elemental conditions required for analysis. In some circumstances the instrument can compensate for these effects or eliminate them. In some situations, however, each effect has to be determined prior to the analysis. Potential sources of error are:

- Background Absorption
- Tube Contamination
- Solution Contamination (reagents, containers, modifiers)
- Memory
- Incandescence
- Elemental Emission

Background Absorption

Causes and effects of background absorption have been described in Chapter Three, and the Zeeman technique for background correction has been described in Chapter Two. Generally, it is preferable to exploit temperature programming, chemical modification or both rather than relying solely on background correction.

When first establishing a temperature program, an important objective is to obtain ashing parameters which selectively volatilize the matrix without loss of analyte, thereby removing those matrix components which cause background absorption. Alternatively, adjust the temperature program to create a time lapse between the background signal and the analyte signal such that the two signals are separately observed. If these options are not practical, it may be necessary to use matrix modification (refer to Chapter One).

Tube Contamination

Traces of some elements may be present in new graphite tubes as a consequence of the manufacturing process. These trace elements must be removed before the tubes are used for analysis. Tubes can be readily decontaminated by using the 'Tube Clean' facility two or three times. This raises the temperature of the tube to 2700 °C, thereby removing most of the impurities. For elements which require an atomization temperature greater than 2700 °C, the tube should be decontaminated at the recommended atomization temperature (see Chapter Four). Repeat this process until a constant blank level is obtained.

Solution Contamination (Reagents, Containers, Modifiers)

Contamination at either the reagents, chemical modifier or the container must be removed prior to the analysis. Methods for this have been described previously. Always remember that furnace techniques are for trace metal analyses: therefore cleanliness is essential. A reagent blank must always be included in the analytical program.

Memory

A number of elements form stable refractory carbides within the graphite tube atomizer and thus some of the element remains in the graphite tube after atomization. Consequently, during the next determination there is a residual signal, or memory effect. Elements such as titanium, strontium and vanadium are known to form these refractory carbides. To reduce these effects, either the atomization time can be increased or a tube clean program can be included at the end of the analytical program.

Incandescence

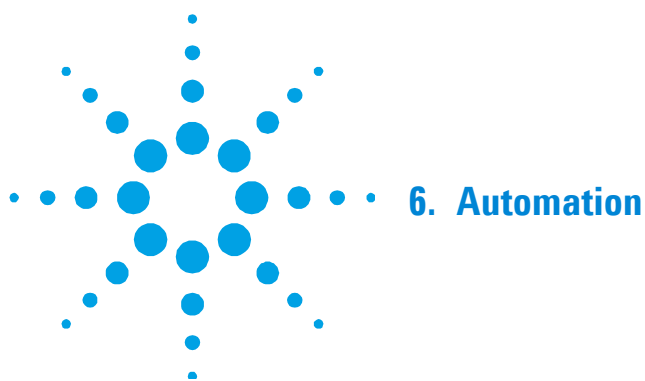
This is discussed more fully in Chapter Three. Generally it can be said that incandescence is rarely a problem and is only likely to be encountered with elements for which the atomization temperature is high but the lamp intensity is relatively low. In this circumstance, the light source intensity must be increased relative to the tube emission intensity. This can be achieved in a number of ways:

- Increase the hollow cathode lamp operating current
- Use the special reduced-height slit
- Reduce the spectral band width
- Decrease the atomization temperature

Elemental Emission

This has also been referred to in Chapter Three and again it can be said that this phenomenon is encountered infrequently in practice. Some elements, however, may give problems with element emission in which case decreasing the atomization temperature may be helpful. If possible, an alternative ground state line outside the emission band should be used (preferably below about 350 nm).

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6. Automation

There are three major reasons for automating furnace analyses:

- To improve analytical precision
- To increase analytical productivity
- To release staff for other tasks

The following table shows the precision obtained manually and automatically.

Table 6 Analytical precision for successive groups of 10 injections

| | Manual Dispensing (%RSD) | Automatic Dispensing (%RSD) |
|---------|--------------------------|-----------------------------|
| Group 1 | 3.1 | 2.2 |
| Group 2 | 2.5 | 1.8 |
| Group 3 | 2.7 | 2.1 |
| Group 4 | 3.7 | 2.1 |

Automated dispensing produces better results because:

- The drop is always dispensed at the same spot in the graphite tube.
- The sample dispenser does not suffer from operator fatigue.
- Automatic dispensing is consistent.

Although the idea of automated analysis is associated with large numbers of samples it has significant advantages for one sample. Setting up the graphite tube atomizer and sampler takes only 2 minutes and is therefore fast enough to make this practical.

The average time for one complete determination is 3 minutes. To analyze a blank, three standards and one sample will thus take about 20 minutes. If each solution is analyzed in duplicate the time will increase to 40 minutes. The analyst can use this time to carry out other tasks.

Programmable Sample Dispenser

Each carousel has fifty numbered positions in two rows at the periphery. Numbers 1 to 45 are for the samples, 46 to 50 are for premixed standards (1 to 5). In the center are three positions; blank (position number 0); standard or reslope solution (position number 51); chemical modifier (not numbered).

Up to four solutions (each separated by an air slug) can be drawn into the capillary. They are then dispensed directly into the graphite tube where they mix. This is particularly useful when premixing is undesirable - as for example when precipitates are formed.

The order of pick-up of solutions is set to obtain the best precision. For NORMAL CALIBRATION the order is BLANK, MODIFIER and STANDARD or SAMPLE. This means the blank is the last solution dispensed and 'washes out' the capillary ensuring all the standard or sample is dispensed into the tube. For STANDARD ADDITIONS CALIBRATION the order is BLANK, MODIFIER, STANDARD and SAMPLE. The blank is the last solution dispensed and as before ensures all the standard and sample solution is transferred into the tube. A minimum volume of 5 μL should be used for the blank.

The volume of each solution drawn into the capillary can be varied to suit the particular analytical requirements. The maximum volume which can be dispensed is 70 μL .

Before the capillary is dipped into the first solution, the syringe system automatically draws an air slug into the capillary. The capillary then dips into each selected solution in turn, separating each solution by an air slug.

The system ensures that the dispensing volume is accurately controlled as the precision of the analysis depends upon this. The sample dispenser uses a syringe driven by a linear stepper motor under microcomputer control, thus repeatability is ensured. A PTFE capillary is used to pick up the solutions thus ensuring that contamination is minimized.

A 500 mL polythene bottle attached to the sample dispenser contains rinse solution. The bottle is pressurized with inert gas through the NORMAL inlet and it is essential that inert gas is always supplied to the graphite tube atomizer even when ALTERNATE gas has been selected for every stage of the furnace program. For the rinse solution, always use distilled water acidified with nitric acid to give a concentration of 0.01% by volume. It is also desirable to add a small quantity of Triton X-100 to give a concentration of 0.005% Triton by volume, but other solvents can be used, provided they have no effect on the polythene bottle or stainless steel plunger of the glass syringe. All other components which are in contact with the rinse solution are made of PTFE or modified PTFE.

Before starting an analysis it is good practice to press RINSE (on the SAMPLER page) and TUBE CLEAN (on the SIGNAL GRAPHICS page). This ensures:

- The sampling capillary is rinsed and clean.
- The tube surface is cleaned and the tube is brought to its ambient operational temperature.

While the rinse is taking place the operator should check that there are no air bubbles in the syringe or PTFE capillary. If air bubbles are present in the syringe this should be carefully removed from the sample changer. Press RINSE soft key and withdraw the syringe plunger, holding the syringe body at an angle to allow the air bubbles to rise and be washed out of the syringe. Press RINSE again and while the rinse solution is flowing replace the plunger. When the rinse cycle has finished replace the syringe carefully in the sample changer.

Setting up the Capillary

A mirror is supplied to enable the operator to see inside the graphite tube. This should be positioned towards the rear of the right hand-side of the burner shield. The mirror can be rotated and slid up and down the stainless steel shaft to a position convenient to the operator. The mirror is counter balanced so that when released by the operator it swings out of the optical path.

Capillary Set Up

The objective is to ensure that:

- The capillary is correctly located in the vials when picking up solution.
 - The capillary enters and leaves the graphite tube atomizer without touching the sides of the injection hole.
- 1 Ensure that the sampler is correctly installed as described in the operation manual. Ensure that the graphite tube atomizer is correctly aligned in the optical path as described in the operation manual.
 - 2 On the INSTRUMENT PARAMETERS page select SAMPLER PREMIXED for the means of SAMPLE INTRODUCTION.
 - 3 Select the SAMPLER page. This page provides access to the ALIGN SAMPLER soft key which allows you to operate the sampler arm without dispensing solutions.
 - 4 Place a clean, dry microvial in the dispenser carousel at position 1.
 - 5 Press ALIGN SAMPLER.
 - 6 The sampler will position the capillary at sample number 1 In the fully down position.
 - 7 Refer to Figure 24 and adjust the capillary as follows:
 - a By releasing clamp 1 you can adjust the height of the capillary and set the capillary so that it is vertical in one plane. By releasing clamp 2 you can set the capillary vertically in the other plane.
 - b Set the capillary so that it is vertical and in the center of the microvial. The tip should be near, but not touching, the bottom of the microvial. Ensure that the black sleeve on the capillary will not be immersed.

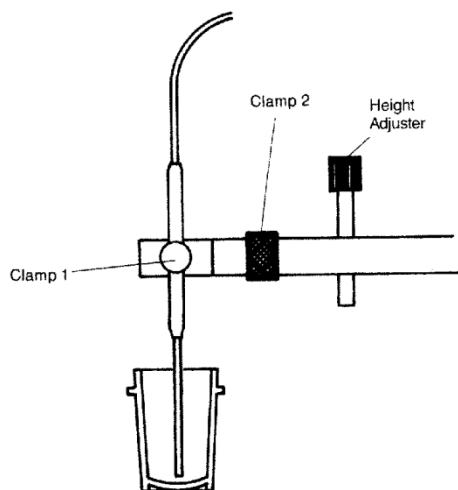


Figure 24. Location of capillary clamps and height adjuster

- 8 Press ALIGN SAMPLER and watch the sampling arm. Place a finger under the arm as it starts to descend into the furnace and gently lower the arm by hand. Note the position of the capillary relative to the injection hole in the graphite tube atomizer. Carefully adjust the sampler position using the sideways adjuster and the fore-and-aft adjuster (Figure 25) so that the capillary is exactly in the center of the sample injection hole.

With the capillary correctly centered it should now be possible to lower the capillary into the graphite furnace (it may be necessary to alter the setting of the height adjusting screw to allow the capillary to descend freely).

- 9 With the capillary down in the furnace, use the height adjusting screw (Figure 24) to set the capillary so that it is about 1 mm above the bottom of the tube. Note that it may be necessary to re-adjust the height of the capillary during method development (see Capillary Adjustment Notes below).
- 10 Check the alignment and operation of the capillary as follows:
 - a Press ALIGN SAMPLER. The sampler will return the capillary to the rinse position.
 - b Press ALIGN SAMPLER and observe that the capillary dips correctly into the sample vial at position number 1. If the adjustment is not correct, repeat instruction 7.
 - c Press ALIGN SAMPLER. The arm will swing over to the furnace and the capillary should descend into the sample injection hole without touching the sides. If the adjustment is not correct, repeat instruction 8.

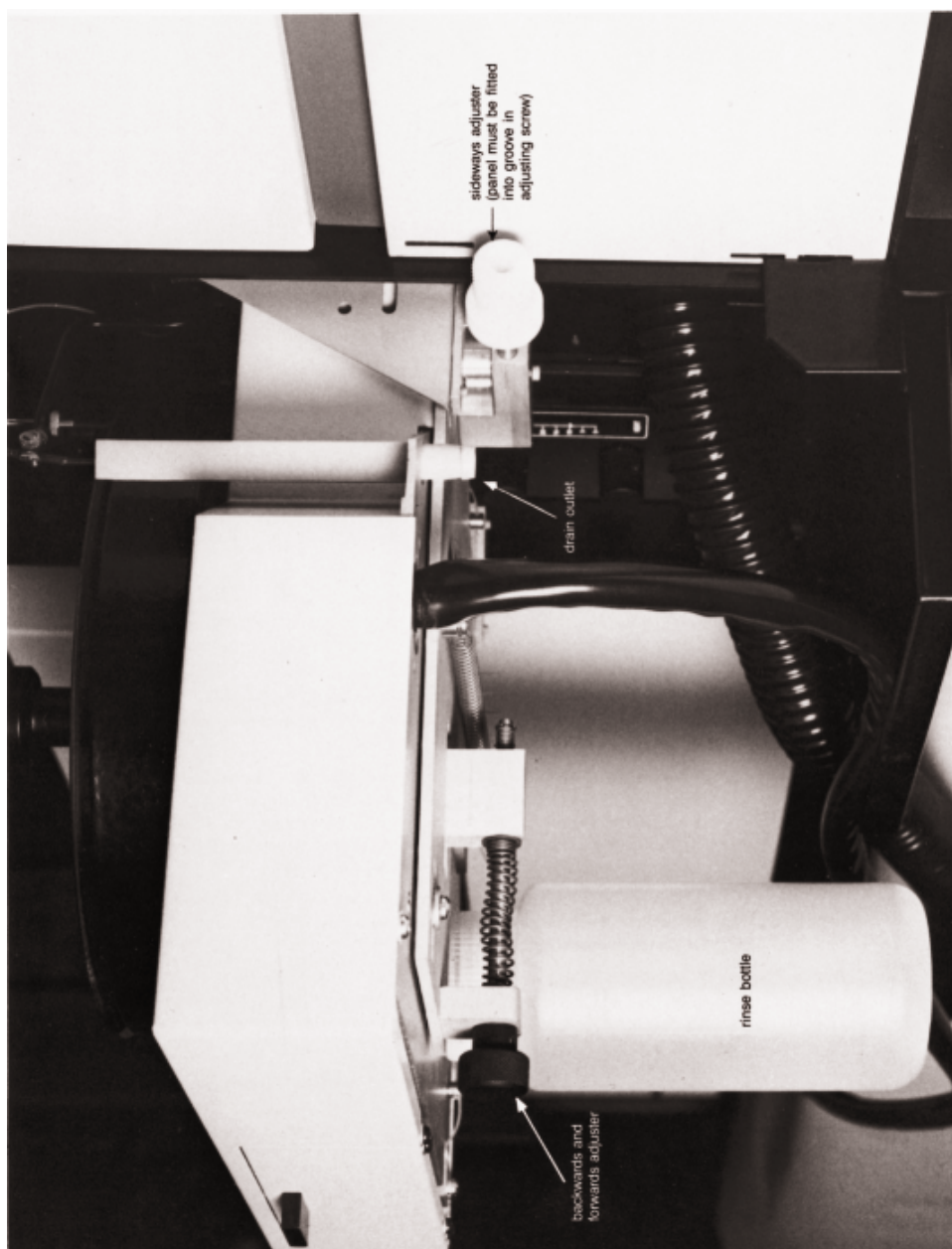


Figure 25. Location of sampler position adjusters

Capillary Adjustment Notes

When establishing optimum operating parameters (furnace program and dispensed volumes, for example), you should also ensure that the droplet is being properly dispensed into the furnace.

For some analyses, the height to which the capillary is set within the tube may be critical, and analytical precision may ultimately depend on reproducible placement of solution in the atomizer.

The actual setting required will depend on the physical characteristics of the solution and the volume of solution dispensed. You may need to re-adjust this for each different analytical situation and some trial-and-error may be necessary to obtain the optimum setting.

While carrying out the necessary trials, you may use the mirror to observe the placement of the droplet within the furnace.

The general procedure is:

- 1 Using suitable furnace and sampler parameters, press START GTA, observe the formation of the drop of liquid on the capillary tip, and adjust the height of the capillary if necessary.
- 2 Ensure that the droplet always touches the bottom of the graphite tube before the injection is completed, otherwise the liquid may climb up the outside of the capillary and block the sample injection hole.
- 3 For large volumes, avoid setting the tip too low, otherwise the droplet may climb up the outside of the capillary and block the sample injection hole.
- 4 Allow the graphite tube atomizer to complete the temperature program and note the analytical signal.
- 5 Repeat the procedure as often as required to obtain optimum analytical response coupled with acceptable analytical precision.

As a guide the capillary should be close to the surface for organic solvents. For aqueous solutions the tip should be positioned as described above, its height being dependent upon the volume dispensed.

Programming the Sampler

The CALIBRATION mode is selected on the METHOD page and can be NORMAL, STANDARD ADDITIONS or BRACKETING STANDARDS.

The Sampler Changer can be operated in either the PRE-MIXED mode or the AUTOMIX mode.

The mode is selected on the INSTRUMENT PARAMETERS page. The calibration and sampler modes automatically define which sampler page is displayed.

Operation (Normal Calibration)

| | Concentration | | Sampler Premix |
|------------|-----------------------------------|-------|----------------|
| | Sampler Volumes (μL) | | |
| | Solution | Blank | Modifier |
| Blank | — | 25 | 5 |
| Standard 1 | 20 | 5 | 5 |
| Standard 2 | 20 | 5 | 5 |
| Standard 3 | 20 | 5 | 5 |
| Standard 4 | 20 | 5 | 5 |
| Standard 5 | 20 | 5 | 5 |
| Sample | 20 | 5 | 5 |

RECALIBRATION RATE 20

RESLOPE RATE 0

MULTIPLE INJECT NO

HOT INJECT NO

PRE INJECT MOD NO

NOTE

The sampler is programmed to a constant volume.

The sequence followed by the sample dispenser is:

- 1 Pick up 25 μL of blank and 5 μL of chemical modifier, then dispense both solutions into the graphite tube. The analyte concentration is then measured.
- 2 Pick up 5 μL of blank, 5 μL chemical modifier and 20 μL of standard 1 solution. All three solutions are dispensed into the graphite tube and the analyte concentration determined. This step is repeated for the other standards.
- 3 Finally, pick up 5 μL blank, 5 μL chemical modifier and 20 μL of sample, dispense all three into the graphite tube and determine the analyte concentration. This is repeated for each sample.

The order of pick up of the solutions ensures that the blank washes out all the standard or sample solution. This contributes to better precision.

After dispensing each set of solutions into the graphite tube the capillary tip is automatically moved to the rinse vessel where it is washed internally and externally, thus ensuring that cross contamination is virtually eliminated.

It is not obligatory to dispense three solutions. Use of a chemical modifier will be dictated by the sample matrix. It is preferable to use a small volume of a concentrated solution of chemical modifier as this allows larger volumes of sample to be used.

Use of blank, to work at constant volume, is always recommended as this allows best precision to be obtained. A minimum volume of 5 μL is recommended. However, if chemical modifier has been programmed, this can be used to 'wash out' the sampler capillary instead of blank.

Operation (Standard Additions Calibration)

| | Concentration | | Sampler Premix |
|------------|----------------------|-------|----------------|
| | Sampler Volumes (µL) | | |
| | Solution | Blank | Modifier |
| Blank | — | 25 | 5 |
| Standard 1 | 20 | 5 | 5 |
| Standard 2 | 20 | 5 | 5 |
| Standard 3 | 20 | 5 | 5 |
| Standard 4 | 20 | 5 | 5 |
| Standard 5 | 20 | 5 | 5 |
| Sample | 20 | 5 | 5 |

RECALIBRATION RATE 1

| | | | | | |
|---------------------|------------|-------------|----------------|---------------|---|
| MULTIPLE INJECT YES | HOT INJECT | YES | PRE INJECT MOD | YES | |
| NUMBER | 2 | TEMPERATURE | 85 | LAST DRY STEP | 3 |
| LAST DRY STEP | 5 | INJECT RATE | 1 | | |

The sequence followed by the sample dispenser is as follows:

- 1 Pick up specified volumes of blank and chemical modifier; dispense both solutions into the graphite tube. The analyte concentration is then measured.
- 2 Pick up specified volumes of blank, chemical modifier, standard solution and finally sample 1. The four solutions are dispensed into the graphite tube and the analyte concentration measured. This is repeated for additions 2, 3, 4 and 5.
- 3 Pick up specified volumes of blank, chemical modifier, and sample 1 The 3 solutions are dispensed into the graphite tube and the analyte concentration measured.
- 4 Steps 1, 2 and 3 are repeated depending upon the re-calibration rate programmed.

The capillary is rinsed after each dispensing cycle as previously described. The use of blank and chemical modifier with each standard addition is determined by analytical requirements.

Calibration

Three methods of calibration are available, NORMAL, STANDARD ADDITION and BRACKETING STANDARDS.

Normal Calibration

This mode would be selected when the sample composition is known or the matrix is simple. Up to five standards may be used, depending upon the analytical requirements.

Preparation of Standards

Standards may be prepared by either of two methods: Premixed Standards or Dispensed Standards.

Premixed Standards

These standards are prepared in the usual manner in the laboratory and are placed in positions 46 to 50 of the carousel in ascending order of concentration.

Example

A calibration scheme consisting of three standards 0.005 µg/mL, 0.01 µg/mL and 0.015 µg/mL is required. These standards are made by the analyst and placed in positions 46, 47 and 48 in the carousel.

Generally it is preferable to use constant volumes (standards and samples use the same volume). In this example a volume of 20 µL has been selected. Note 5 µL of blank has also been specified to 'wash out' the capillary. If higher analytical signals are required then greater volumes (up to 70 µL total) can be injected. For larger signals see 'Multiple Injection'.

The analyst then enters the required volumes through the numerical keyboard. The visual display will appear as follows:

| | Concentration | | Sampler Premix |
|------------|----------------------|-------|----------------|
| | Sampler Volumes (µL) | | |
| | Solution | Blank | Modifier |
| Blank | — | 25 | 0 |
| Standard 1 | 20 | 5 | 0 |
| Standard 2 | 20 | 5 | 0 |
| Standard 3 | 20 | 5 | 0 |
| Sample | 20 | 5 | 0 |

RECALIBRATION RATE 16

RESLOPE RATE 0

MULTIPLE INJECT NO

HOT INJECT NO

PRE INJECT MOD NO

The data produced is processed by the AA instrument to give a concentration figure which is recorded on a floppy disk and printed out.

Dispensed Standards

These are produced by the sample dispenser from one standard solution but using different volumes. The standard solution is placed in position 51 in the carousel. The operator enters the volume to be taken from the solution in the table on the V.D.U. for each standard.

Example

A calibration scheme consisting of three standards, 0.005 µg/mL, 0.01 µg/mL and 0.015 µg/mL is required.

The operator places a 0.005 µg/mL solution in position 51 of the carousel. The volumes required for standards of 0.005, 0.01 and 0.015 µg/mL are in the ratio 1:2:3. Thus if 10 µL are taken for standard 1, then 20 µL and 30 µL must be taken respectively for standards 2 & 3.

The operator then decides if chemical modifier is to be used and works at constant volume by adding blank solution. It is also necessary to decide on the total volume to be added per injection, which must not exceed 70 µL.

In this example 5 µL of chemical modifier and constant volume will be used.

| | Concentration | Sampler Automix | |
|------------|----------------------|-----------------|----------|
| | Sampler Volumes (µL) | | |
| | Solution | Blank | Modifier |
| Blank | — | 30 | 5 |
| Standard 1 | 10 | 20 | 5 |
| Standard 2 | 20 | 10 | 5 |
| Standard 3 | 30 | 0 | 5 |
| Sample | 30 | 0 | 5 |

RECALIBRATION RATE 20

RESLOPE RATE 0

MULTIPLE INJECT NO

HOT INJECT NO

PRE INJECT MOD NO

NOTE

As modifier is the last solution dispensed it washes out any traces of standard or sample remaining in the capillary, thus BLANK is not required for the top standard or samples. Keeping the total volume as low as practicable shortens the drying time and hence the overall analysis time. If PRE-INJECT MODIFIER is programmed then BLANK must be programmed for all solutions.

Standard Additions Precautions

There are limitations to the standard additions technique, and all the limiting factors should be considered. These limitations are:

- The method assumes that the analyte in the standard added reacts identically to the analyte in the sample. This is not valid for all analyses. Standards added as nitrate may not behave in exactly the same way as organically-bound analyte in the sample, for instance. The accuracy of the method should be checked using a completely independent sample preparation (e.g. digestion or ashing) to verify the accuracy of the results.
- The sample absorbance and all the absorbance values for the additions series must be in a linear part of the calibration graph (establish the calibration up to a maximum of about 0.4 ABS).
- Background absorption is not corrected in this technique, and must be deducted from all measurements by using a background corrector.
- One set of additions should be prepared for each sample type because different effects will occur with different matrices.

Standard Additions Calibration

When samples of greater chemical complexity are analyzed, other techniques become important. It may be necessary to prepare chemically matched standards so that the decomposition behavior of standards and samples will be comparable and this will become increasingly difficult for more complex samples. Such factors as the sample viscosity, dissolved salt content and potential interfering species must be considered.

For very complex samples it is still possible to use simple aqueous standards. This generally is true when the matrix can be completely removed with appropriate temperature programming before atomization, but there is no universal rule to identify these situations.

In the standard additions method a number of equal aliquots of sample are taken and diluted, with the addition of increasing quantities of the analyte, to a particular volume. These are analyzed in the graphite tube and a calibration graph is constructed as shown in Figure 26.

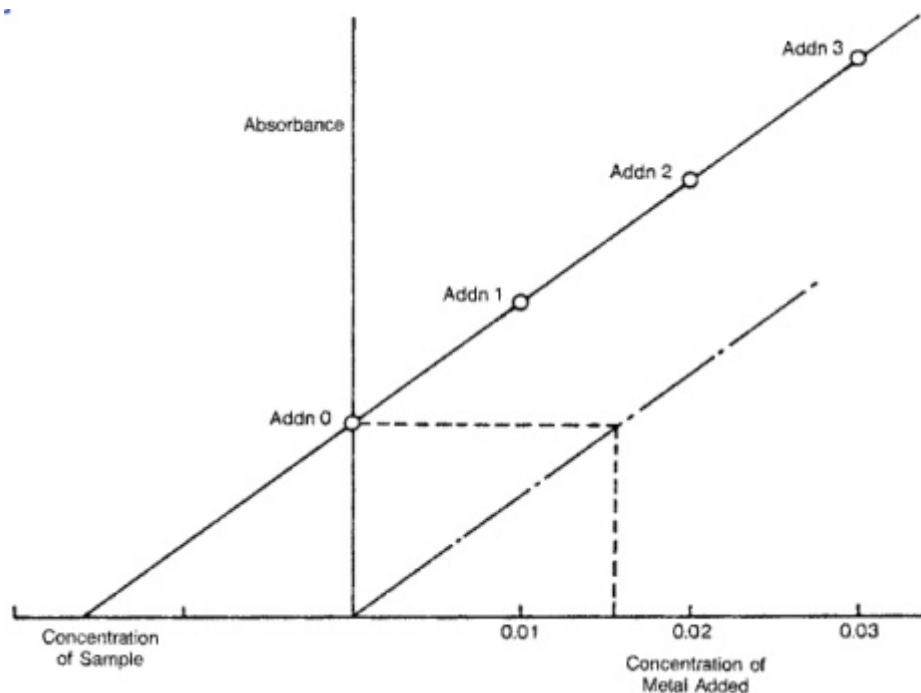


Figure 26. Standard additions graph

This procedure has three immediate benefits:

- By construction of the graph and extrapolation to zero absorbance, the concentration of analyte in the standard additions sample can be determined from the intercept on the concentration axis.
- When the slope of the graph is the same as the slope of the normal calibration graph for simple aqueous standards, it can be assumed that chemical interference is negligible (but there are limitations to this assumption). See Figure 26.
- If there is a definite interference and the slope is not the same as for aqueous standards, the additions series itself can be used as a set of calibration standards for samples, provided the matrix is the same in every sample.

Example

Ten unknown samples with complex matrices have been received for trace elemental analysis. The analyst obviously decides to use STANDARD ADDITION ANALYSIS to overcome any unknown matrix problems. He measures a couple of samples normally, to get an idea of the concentration of the analyte, From this he decides to make 4 addition standards for each sample.

The analyst decides he will use 25 μL of sample; 5 μL of chemical modifier, additions of 5, 10, 15 and 20 μL of standard; blank to make up to a constant volume.

These figures are entered into the standard addition table as follows:

| | | Standard Additions | | Sampler Automix |
|------------|----------|----------------------------------|-------|-----------------|
| | | Sampler Volume (μL) | | |
| | Standard | Sample | Blank | Modifier |
| Blank | — | — | 45 | 5 |
| Addition 1 | 5 | 25 | 15 | 5 |
| Addition 2 | 10 | 25 | 10 | 5 |
| Addition 3 | 15 | 25 | 5 | 5 |
| Addition 4 | 20 | 25 | 0 | 5 |
| Sample | — | 25 | 20 | 5 |

RECALIBRATION RATE 1

MULTIPLE INJECT NO HOT INJECT NO PRE INJECT MOD NO

As the analyst wishes to apply the standard addition calibration to each sample individually, RECALIBRATION RATE is set to 1. The analyst loads the ONE standard solution into position 51 in the carousel and the samples into positions 1 to 10, presses START and the system carries out the analysis.

Standard Additions Calculation

This is a simpler and quicker method which can only be used for samples which are chemically and physically similar. The similarity must be such that the calibration established from one set of addition standards is analytically valid for all the samples to be analyzed. If the samples do not meet the similarity criteria each individual sample must be analyzed separately against a set of standards which are specific for that sample.

Example

Ten water samples have been taken from a river over 10 hours. Another 10 sea water samples have been taken from a river estuary. As these have different matrices two calibrations must be established. The water samples are placed in positions 1 to 10 and the sea water samples in positions 11 to 20. A re-calibration rate of 10 is specified. A standard addition calibration is produced using sample 1 and this is applied to samples 2 to 10. The system then produces another calibration using sample 11 and applies this to samples 12 to 20.

The STANDARD ADDITION table would appear thus:

| | | Standard Additions | | Sampler Automix |
|------------|----------|----------------------------------|-------|-----------------|
| | | Sampler Volume (μL) | | |
| | Standard | Sample | Blank | Modifier |
| Blank | — | — | 35 | 5 |
| Addition 1 | 5 | 20 | 10 | 5 |
| Addition 2 | 10 | 20 | 5 | 5 |
| Addition 3 | 15 | 20 | 0 | 5 |
| Sample | — | 20 | 15 | 5 |

RECALIBRATION RATE 10

MULTIPLE INJECT NO HOT INJECT NO PRE INJECT MOD NO

Other Advantages of Automated Dispensing

Until now we have only considered single injections, one reading per sample, injection at ambient temperature and simultaneous injection of modifier. Each of these parameters can be varied on the sample dispenser to suit the analytical requirements.

Injection Temperature

Aqueous solutions are normally dispensed onto the graphite tube at ambient temperature. When organic solvents are used, having a lower surface tension, they tend to 'creep' within the tube.

This can be overcome by injecting onto a warm tube, whereby the solvent evaporates rapidly and hence will not creep. Obviously if the tube is too hot the solvent will boil and spatter the dissolved solid material within the furnace. The analyst must therefore choose the injection temperature carefully by experiment. A reasonable starting temperature is half the boiling point of the organic solvent.

- 1 Place pure solvent in sample position 1 in the carousel, as an example use xylene (Boiling Point 140°C).
- 2 Press PAGE on the graphite tube atomizer to bring up the sampler parameter table.
- 3 Move the cursor to HEATED INJECTION and using the HOME key change NO to YES.
- 4 Move the cursor to TEMPERATURE and enter 70 (half the boiling point).
- 5 Press START GTA on the control panel and using the mirror watch the dispensing of the drop.

The injection temperature can be increased by small steps until the analyst is satisfied with the performance. The optimum temperature can then be written into the analytical method and stored.

Organic solvents used should preferably have a high boiling point. If they are slightly water soluble this is advantageous as a water rinse can be used for the capillary. Suggested solvents are di-iso-butyl ketone and xylene. Tetrahydrofuran has advantages because it is water soluble although the boiling point is low. For overnight analytical operation di-iso-butyl ketone is recommended.

Injection Rate

The injection rate can also be changed, the fastest is 1 and slowest 45 (30 μL will be dispensed at rate 1 in 3 seconds and 63 seconds at rate 20). If a solvent creeps very badly then a slow injection can be used. This allows the solvent to be partly evaporated while the injection is taking place, reducing the total volume and maintaining the drop in the center of the tube.

Increasing Analytical Signal

Normally a sample volume of 20 μL is recommended. If the analyte concentration in the sample is very low a larger sample volume (up to 70 μL in a single injection) can be used. If the signal is still small then multiple injection can be used.

Multiple Injections and Last Dry Step

For some analyses, it is advantageous to enhance the analytical signal by using the multiple injection technique. Each aliquot (up to 70 μL) can then be dried, or dried and ashed by appropriate programming (see Chapter Four). Up to 99 multiple injections can be used for any one standard or sample.

For complex samples, some ashing must be included in the 'drying' program to prevent buildup of excessive matrix in such a multiple injection program.

The calibration for silver, for example, shows that adding standards as multiples of 10 μL droplets produces a linear graph over a wider range than standards added as one total volume (see Figure 27). Using several small aliquots allows the total solution volume to be deposited in a smaller area on the tube surface.

A further advantage of multiple injections is obtained with samples of unknown concentration.

Example

The analyst has been given a sample and asked to determine the concentration of chromium which is believed to be about 10 $\mu\text{g/L}$. The sample is prepared on the assumption that the concentration will be about 10 $\mu\text{g/L}$. On analyzing the prepared sample a very small absorbance signal is obtained.

All the analyst needs to do is enter a figure for MULTIPLE INJECTION which thereby increases the analytical signal to the required level.

Pre-injection of Chemical Modifier

For some analyses it is advantageous to pre-inject the modifier. Some elements form strong carbides with the graphite and pre-injection of modifier can tie up the active sites on the surface, reducing carbide formation.

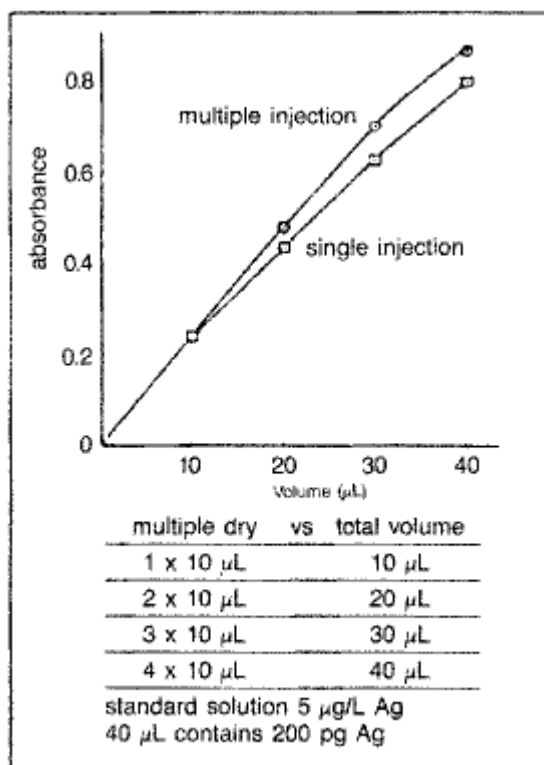


Figure 27. Calibration for silver

Replicates

The provision of replicate analysis (up to 99) allows the analyst to evaluate his proposed method statistically. On a routine basis it may be used to produce a mean result if method development has shown that for a particular type of sample the standard deviation is large. In furnace analysis occasionally a 'wild' result is obtained. By measuring three replicates on each solution any 'wild' result is easily highlighted. Remember that the use of REPLICATES and MULTIPLE INJECTION will increase the total analysis time.

Reslope Rate

It is good analytical practice to run calibration checks during the analysis of a batch of samples. The frequency of these calibration checks (RESLOPE or RECALIBRATION RATE) will be determined by several factors in the laboratory such as temperature, humidity, air flow, boiling point of solvent.

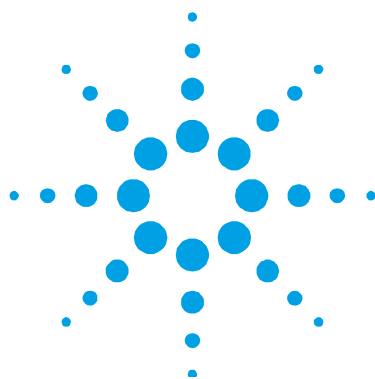
When using organic solvents rather than aqueous solutions, evaporation will be even greater. This will increase the effective concentration of the samples and standards. Thus a RESLOPE which adjusts the calibration slope should be included at appropriate intervals.

Another advantage of reslope is as an early indication of tube failure. When the pyrolytic coating breaks down, solution will soak into the bulk graphite. This causes the analytical signal to be drastically reduced (at least by half), thus when a programmed reslope is performed a reslope error will occur and the system will stop.

Single Sample

Upon inspection of results the analyst may wish to check a sample or standard. This can be done in both NORMAL and STANDARD ADDITION calibration modes. Go to ANALYTICAL RESULTS page and press NEXT SAMPLE soft key until the required sample or standard number is displayed in the common block. Press START GTA and the relevant solution will be processed.

If a calibration check is required in NORMAL CALIBRATION mode before running the samples then a slightly different procedure is used. Ensure the system is in AUTOMATIC RUN mode and enter the same sample number for both FIRST and LAST SAMPLE. Press START and the system will run through the calibration routine and then analyze the sample.



7. Analytical Methodology

Analytical programs developed for a Varian GTA graphite tube atomizer, would normally be entirely suitable for use with the Varian Zeeman graphite furnace. A number of methodologies in this chapter were developed on the GTA-95 or GTA-96.

The data in this chapter is intended as a guide in the selection of appropriate operating conditions for the Zeeman graphite tube atomizer. Operating conditions may be different to some degree depending on the nature of the sample and the chemical form or state of the analyte element.

Whenever your sample differs from the matrices quoted here, it will be essential for you to thoroughly investigate the behavior of your sample in the graphite tube atomizer so that optimum conditions can be established. Additional guidance for selection of operating parameters is given in Chapter Three; information about chemical modifiers will be found in Chapter One; the fundamentals of sample and standard preparation are discussed in Chapter Five.

Practical Operational Hints

- 1 Selection of the best drying parameters for the dispensed sample volume is an important criterion in achieving satisfactory precision. The droplet should dry smoothly without vigorous boiling.

With aqueous solutions best drying conditions have been achieved by ramping to a temperature of about 85 °C in 5 seconds and then applying a slow ramp to about 95 °C. It is possible to dry the aqueous sample smoothly with a maximum gas flow at a temperature below the boiling point with an extended dry time.

For other solvents it is recommended that a 5 second ramp to a temperature of about 60% to 70% of the boiling point be followed by a slow ramp to about 90% of the boiling point and this temperature maintained with maximum gas flow until drying is completed. Alternatively, the solvent may be conveniently injected onto a pre-heated tube and dried virtually on contact.
- 2 Droplet drying should always take place on the internal section of the graphite tube for best precision. If the liquid spills over the internal partitions, the resultant spread of the liquid will cause variability in the analytical signal. If the liquid is a corrosive acid and the dispensed volume is so great that the liquid spreads to the ends of the graphite tube, it may result in corrosion of nearby metal components.

If the pyrolytic platform is used it must be ensured that the droplet remains within the platform and does not spill over onto the graphite tube wall. The droplet should dry smoothly. Use of the mirror supplied will assist the correct choice of drying parameters to ensure this does not occur.

- 3 The dispensed volume itself must not be so great, or deposited in such a manner, that the sampling hole is blocked. In this event the windows may become covered in condensate from the drying step. The gas should always be flowing during the drying stage, preferably at maximum flow, to remove the drying or ashing products.
- 4 20 seconds is automatically allocated for the cool down period after completion of the atomization program. This will ensure cooling of the graphite to within 10 °C of the cooling water temperature, before the next sample is introduced.
- 5 Gas Flows: The flow should be kept high (3 L/min) during the drying period to remove solvent etc. If air ashing is employed, the flow should be sufficient to remove ashing products but should not continue when the temperature approaches 500 °C.

The presence of air will result in excessive corrosion of the pyrolytic graphite at temperatures greater than about 500 °C. At higher temperatures the corrosion rate is greatly accelerated. It is recommended that the inert gas flow is not stopped during atomize for longer than about 6 - 7 seconds. This will normally allow sufficient time to measure the true peak.

The inert gas flow should always be recommenced after the peak has been completed if gas stop is used during atomization. This will help protect the graphite tube. Remember that the maximum gas flow automatically commences on completion of the program and extends for 20seconds, to ensure that the hot graphite is protected during cool down.

- 6 The quartz windows should be inspected at regular intervals to ensure that they are clean. They may be cleaned with a tissue and alcohol, and wiped dry.
- 7 It is always good practice to choose an analytical program which minimizes the amount of background (or non-atomic) absorption during atomization. It is always recommended that the background corrector be on for analytical measurements.
- 8 The use of chemical (or matrix) modifiers in modern graphite furnace analyses is widespread (see also Chapter One). The signal graphics facility will be of great benefit in establishing the correct amount of modifier and most suitable furnace program for your analysis.
- 9 The most suitable analytical wavelength for the Zeeman graphite furnace determination of each element has been given in Chapter Four. This has been based on the analytical sensitivity, MSR% and linearity of calibration (see also Calibration Procedures, Chapter Five).

If other wavelengths are used, it will be necessary to establish the maximum absorbance (MAX ABS). Above a defined maximum absorbance the calibration will either asymptote to a constant absorbance value or reflex to lower absorbances. It is essential to establish this MAX ABS value for each wavelength before proceeding with the calibration (see Calibration Procedures, Chapter Five).

- 10 Dynamic range of an analysis: By careful choice of certain parameters, the analytical signal from any analysis can be varied considerably. For example, the signal may be increased by:
 - a Using argon rather than nitrogen as the inert gas
 - b Using gas stop during atomize, rather than gas flow (the gas flow can be varied from 0-3 L/min.)
 - c Using multiple injections prior to atomization
 - d Increasing the injected volume (from 1 to 70 µL)
 - e Using a suitably high ramp rate
 - f Careful choice of a chemical modifier

- g** Conversely, the signal may be reduced by the appropriate selection of the above parameters.
- 11** With furnace atomization, three standards are normally sufficient to establish the analytical curve. One or two standards are quite adequate for many analyses for which the highest absorbance is about 0.5. Most important is the correct selection of the standard values within the analytical range. By using five standards for calibration, the analysis time is extended, and the accuracy of the measurement will not always be improved.
- 12** For the graphite tube, the maximum recommended sample volume, consistent with an acceptably short drying time, would be about 40 μL . Volumes in excess of this may take an unacceptably long drying time, and also show poorer precision. For the graphite platform, the maximum recommended sample volume would be about 20 μL (See Chapter Four.)
- 13** Programmable Sample Dispenser: The PTFE capillary should be treated carefully - if it is bent it may take some time to return to its initial shape. When the multiple injection facility is used, it may be necessary to allow a cool down period before the next injection (from the same sample vial). This cool down period should be incorporated into the program, following the required dry and ash stages.
- The tip should be cleanly cut at 90° . If variable volumes are automatically dispensed during an automated analysis, the capillary tip should be set for the minimum volume dispensed. In this case, the drying time should allow the maximum volume to dry.
- After continuous operation some graphite may appear on the capillary tip. This should be carefully removed by wiping with a tissue. (The dispensing characteristics may change in the presence of this graphite film.)
- 14** It is necessary that the rinse bottle of the autosampler contain about 0.01% by volume of nitric acid for work with aqueous solutions. It may be beneficial to also add 0.005% by volume of Triton X-100 for some samples such as biological solutions or organic solvents.
- 15** The normal (inert) gas used in these studies was argon. It is used in preference to nitrogen.
- 16** Graphite tube lifetime: There are many factors which affect the useful lifetime of a pyrolytic coated graphite tube. Among these are the sample type, matrix composition, program temperature, total gas stop time and type of inert gas.
- It has been found that materials such as perchloric acid, perchlorates, sodium nitrate and ammonium nitrate adversely affect the coating, and high concentrations of these materials tend to reduce tube lifetime. The higher the programmed temperature the shorter is the useful tube lifetime. Argon provides better protection for the graphite than nitrogen and allows a longer tube life. Argon is the recommended inert gas.

Selection of Analytical Methodology and Techniques

Furnace atomic absorption has been a technique for the determination of trace elements for over a decade and, as a result, there is an immense amount of literature on methods of analysis in a diversity of samples. The most useful sources for these methods have been listed in Appendix 1 and 4 while the Journal 'Progress in Analytical Atomic Spectroscopy' presents review articles by authorities in specific fields embodying comprehensive assessments of analytical techniques and their application.

Many analytical methods are subject to strict analytical procedures resulting from legislation implemented by Governments. If an analytical method is required for compliance with regulations, then the relevant Government department should be consulted for the specific analytical procedure together with any relevant guidelines.

A list of bodies in the USA which have developed specific methods that conform to legislation is given in Appendix 6. The U.S. Government printing office has produced publications detailing acceptable methods of analysis.

With the graphite tube atomizer the sample will usually be presented for determination as a liquid and many samples will require digestion. After digestion or dissolution, the level of the element of interest may be low, or substantial matrix interferences may be encountered. When this occurs the sample may require further treatment prior to determination. The separation of the analyte element from the parent matrix forms the basis to separation and pre-concentration techniques such as solvent extraction and ion exchange. These procedures at the ultratrace level require extreme care, skill and the use of good laboratory practices to gain accurate results.

Optimization of the Ash Stage

Ideally the ash stage should remove all the sample matrix components and leave only the analyte element which, on atomization, will give a single peak. However, some samples contain components which are of similar volatility to the analyte element. These components can cause substantial physical and chemical interferences which, in most cases, can be reduced or eliminated by using:

- Zeeman background correction (see Chapters Two and Three)
- Chemical modification (see Chapters One and Eight)
- Standard additions (see Chapter Five)
- Dilution
- Optimum ash temperatures and times (see Chapter Three and the Petroleum Section in Chapter Seven)

Chemical Modification and Reduction of Interferences

The interfering effects of high concentrations of matrix components on trace metal analysis have been recognized for some time. Early studies reported that there were potential problems due to interferences (279).

Processes which take place in the graphite furnace are complex, and analysts should be aware of this when new samples are analyzed.

The effects of some matrix elements on the analysis of copper and manganese were examined showing that different salts can alter the profile of the atomic peak (280). A comparison of the interference effects for manganese in a constant temperature and a pulsed type furnace has been described (281).

Removal of chloride interference in the determination of chromate ion has been achieved by conversion of the metal chloride to an oxide before the atomization step. Ammonium EDTA was also highly recommended (282) for this problem.

Phosphoric acid has been used extensively for the analysis of cadmium, lead, zinc and copper (6, 36, 33, 30). Thiourea was effective in removing alkali chloride interference from the analysis of copper and manganese in a molybdenum furnace (283).

In recent years the use of chemical modifiers has proved to be a routine procedure for the determination of many elements. A summary is given in Chapter One, and a number of examples are given in Chapter Four.

Digestion Methods

The degree of care taken with the digestion and dissolution of substances into solutions, together with the analytical method employed, determines the precision and accuracy of the result obtained.

Samples requiring digestion for atomic absorption can be classified into either inorganic or organic matrices. Dissolution usually involves the use of mineral acids or a fusion, and depends on the nature of the sample and element of interest. A comprehensive reference covering decomposition methods of both inorganic and organic matrices is given in reference 72. Methods on the destruction of organic matrices have been covered by T. T. Gorsuch (73), and inorganic matrices by J. Dolezal, Z. Sulcek and P. Povendra (74, 75).

Autoclaves and PTFE High Pressure Digestion Vessels

The most recent advances in sample digestion have been concerned with decomposition of samples under pressure in sealed iron or aluminum autoclaves which have PTFE, platinum or gold inserts. The pressure decomposition of substances is based on the heating of the sample and liquid in a closed vessel in which the pressure increases as a result of the increasing temperature. In most cases a mineral acid (or a combination of mineral acids) is used and at higher temperatures and pressures their activity increases, facilitating the dissolution of many substances not digested under normal atmospheric conditions.

Autoclaves containing PTFE inserts are inert to the mineral acids, and have been used extensively for the decomposition of inorganic and organic samples. PTFE autoclaves are ideally suited to furnace applications and have the following advantages:

- Digestion of the sample is faster and more complete as a result of high temperature and pressures.
- The decomposition procedures are easily implemented and only require an autoclave and a hot plate.
- Large numbers of samples can be digested simultaneously, depending on the type of autoclave used.
- Contamination from outside sources is reduced by using a sealed vessel.
- Volatile elements and volatile compounds formed during the digestion process are retained.
- Submicrogram amounts of elements, which may otherwise require large amounts of contaminated fusing agents, can often be digested by small volumes of mineral acids in such an autoclave.
- High pressure autoclave digestions generally yield results which are closer to the true value.

PTFE has been shown to have considerable reducing effects for polyvalent elements such as iron and tin and is not recommended for digestions requiring differentiation between individual valency forms (75). The maximum temperature of operation for PTFE decomposition vessels is 250 °C because distortion and the possible production of toxic substances occurs with PTFE above 300 °C. There are a number of commercially available PTFE high pressure vessels and sealed decomposition vessels and these should be used strictly in accordance with the manufacturer's recommendations (76-80).

Single Acid Digestion of Organic Matrices

With digestions that require wet ashing and when a PTFE digestion vessel is not applicable, the digestion of organic matrices can be achieved effectively with a single acid (81). A simple glass apparatus in conjunction with a burner has successfully been employed to digest a variety of organic matrices for a number of trace elements (Al, B, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, Zn).

Environment

Air Particulates, Dust and Sediments

The role of trace metals in air has been the focus of many studies because of the impact of trace metals on human health. Most metallic compounds in the atmosphere exist as particles or are adsorbed on particulates arising from natural causes or human activities. Particles greater than 1 μm are normally removed by the body's respiratory filter (82), but it has been demonstrated that toxic metals are preferentially concentrated in submicron particles (83, 84) which can enter the lungs. Migration and assimilation of trace metals from the particles can then occur through natural biochemical processes with consequent toxic effects. The development of effective methods of sampling and analyzing atmospheric particulates is thus of great importance in monitoring the environment and eliminating or reducing health hazards.

Analysts confronted with either industrial hygiene or environmental analyses should first determine whether any federal, state or local regulations require specific methodology. In the absence of any official procedures a number of specific references and manuals can be consulted (85-98). Further information covering sampling and analysis of particulates by furnace atomic absorption spectrometry is presented in an extensive review by Nolter, Bloom and Arnold (99). An overview of industrial hygiene covering the legal requirements, regulatory bodies and exposure levels is presented in the application notes 'AA at Work' Number 2, while information regarding the nature of air particulates and specific methods is covered in 'AA at Work' Numbers 3 and 7 (100-102).

Sample Collection

The greatest difficulty with the sampling of particulate matter is the collection of a representative sample. In most situations a large volume of air has to be sampled in order to gain a large enough sample for analysis. Fortunately, because of its high sensitivity, the graphite tube atomizer enables the analyst to use low volume samples. Sublitter sampling has also been achieved using specially designed apparatus and graphite tubes (103-110). A variety of methods are available for collection of air samples, the most common being sedimentation and filtration (99). Sedimentation is mainly employed in the collection of atmospheric samples, while filtration is extensively used in both environmental and industrial hygiene monitoring.

Sedimentation

Sedimentation is the simplest technique for the collection of particulate matter and is generally limited to particles whose diameters exceed 10 μm (82, 85, 91). Collection involves the use of glass jars, metal or plastic cylinders whose height is about 2 - 3 times their diameter, which have been placed in a number of locations for a period of about a month. The sample collected is dependent on the shape, dimensions and height above the ground at the container. Other factors such as algae, fungi, bird faeces and human interference also have an effect upon the sample. Data obtained from fall out studies are not relevant in the elucidation of immediate health problems but are effective in studying the transport of particulates arising from a specific source.

Filtration

Filtration is the most common method of collecting particulate matter and involves drawing of an air sample through a filter. The Environmental Protection Agency (EPA) of the USA specifies the high volume sampler which can sample up to 2500 mL in 24 hours (87, 88). The volume of air and the gain in weight at the filter are measured prior to subsequent analysis by atomic absorption. For the sampling of smaller volumes of air (typically 20 - 200L) a portable battery driven pump is used in conjunction with a cartridge containing a membrane filter.

Low volume sampling has the advantage of checking pollutants that may exceed maximum allowed levels for short periods, such as lead emissions originating from motor vehicles at rush hours. A further advantage is that the sampling equipment is simple and portable. Care has to be taken with low volume sampling techniques because contamination from the filters, reagents and glassware can lead to high blanks (82).

Industrial Hygiene Samples

Two general sample types are used in industrial hygiene evaluations of human exposure, namely area samples and personal samples normally collected on a filter after sampling a known volume of air (92-98). Table 7 lists the Permissible Exposure Limits (mg/m^3) as set by OSHA in June 1979.

Table 7. OSHA PEL* Values for Contaminants Analyzed by AA

| Substance | PEL | Substance | PEL | Substance | PEL |
|---|------------------------------------|--|-------|--|------|
| Antimony and compounds (as Sb) | 0.5 | Hafnium | 0.5 | Selenium compounds (as Se) | 0.2 |
| Arsenic and compounds (as As) | 0.010 (inorganic) 0.5 (organic) | Iron oxide fume | 10.0 | Silver, metal and soluble compounds | 0.01 |
| Barium, soluble compounds | 0.5 | Lead, metal, inorganic compounds and organic soaps | 0.050 | Tantalum | 5.0 |
| Beryllium and compounds | 0.002 | Lithium hydride | 0.025 | Tellurium | 0.1 |
| Cadmium, dust | 0.2 | Magnesium oxide fume | 15.0 | Thallium, soluble compounds (as Tl) | 0.1 |
| Cadmium, fume | 0.1 | Manganese | 5.0 | Tin, inorganic compounds except oxides | 2.0 |
| Calcium oxide | 5.0 | Mercury | 0.1 | Tin, organic compounds | 0.1 |
| Chromium, metal and insoluble salts | 1.0 | Organo (alkyl) mercury | 0.01 | Titanium dioxide | 15.0 |
| Chromium, soluble chromic, Chromous salts (as Cr) | 0.5 | Molybdenum, insoluble compounds | 15.0 | Vanadium, V_2O_5 dust | 0.5 |
| t-Butyl Chromate (as CrO_3) | 0.1 | Molybdenum, soluble compounds | 5.0 | Vanadium, V_2O_5 fume | 0.1 |
| Cobalt, metal, fume and dust | 0.1 | Nickel, metal and soluble compounds (as Ni) | 1.0 | Yttrium | 1.0 |
| Copper, dust and mist | 1.0 | Platinum, soluble salts (as Pt) | 0.002 | Zinc chloride fume | 1.0 |
| Copper, fume | 0.1 | Rhodium, metal fume and dust (as Rh) | 0.1 | Zinc oxide fume | 5.0 |
| Ferrovandium dust | 1.0 | Rhodium, soluble salts | 0.001 | Zirconium compounds (as Zr) | 5.0 |

*Permissible Exposure Limit (in milligrams per cubic meter of air) as of June, 1979.

The Permissible Exposure Limit (PEL) is the maximal average concentration of an air contaminant to which an individual may be legally exposed as promulgated by the Occupational Safety and Health Administration. The PELs are generally stipulated as a Time Weighted Average concentration over normal 8-hour workshift or 40-hour workweek.

Area Samples

Area samples are collected at a selected work site or specific location within the working environment. This stationary sample enables determination of background levels or airborne contaminants which may vary from one location in a work site to another. The efficiency of control equipment can also be evaluated using area samples.

Area samples can also be collected with a portable personal sampling train by placing it in a stationary position in the work zone. Frequently, however, a stationary, high-volume air pump may replace the portable pump, especially if a larger sample is required.

Personal Samples

The personal sample is collected in the 'breathing zone' and is defined as the sphere approximately two feet in diameter surrounding a worker's head. Consequently, this sample best indicates the actual amount of contaminant inhaled by an individual who is mobile throughout the work site.

Instantaneous or 'Grab' Sampling

Sampling for any time period less than five minutes is referred to as instantaneous or 'grab' sampling. Such a short sampling duration only represents the momentary contaminant concentration. Grab samples are suitable for determining airborne contaminant concentrations during several short phases of a cyclic operation. Consecutive samples indicate the variation of concentration with time.

Graphite furnace atomization is ideally suited to grab samples because of the technique's high sensitivity for most elements.

Minimum Sample Volume

Contaminant concentrations may fluctuate during the day or vary in different locations. An analyst can easily determine the minimum sample volume required to obtain a reasonable absorbance by using the characteristic mass given in Chapter Four for the element of interest. A worked example is presented for an industrial hygiene sample in the application note 'AA at Work' Number 3 (101).

In the absence of any stipulated industrial hygiene method, the sample preparation outlined here can be employed for the determination of metals associated with aerial particulates.

Environmental Samples

The collection and analysis of atmospheric particulates has been the subject of a number of articles and reviews (99, 102-110). These articles should be consulted to gain an appreciation of the analytical requirements needed to implement a monitoring program.

The analytical method outlined in this section was carried out by Begnoche and Risby who used a low volume sampling technique and a CRA-63 to analyze particulate matter from ambient air for a variety of elements (Al, Ca, Cd, Co, Cr, Fe, Mg, Mn, Ni, Zn) (89).

The sampling system employed porous polymer filters (47 mm diameter) with a pore size of either 0.05 or 0.1 μm mounted in a polycarbonate holder (111, 112). A sample of air (20-300 L) whose volume was measured by a calibrated rotameter was drawn through the filter by a portable 12 volt carbon vaned pump powered by a rechargeable battery pack.

Preparation of Filters for AA Analysis

MCE air filters are prepared for AA analysis by dry ash, wet ash (or acid digestion) and extraction techniques. Ashing procedures involve decomposition of the filter and organic particulates. Extraction methods involve removal of the substance of interest from the filter. Since the subsequent AA analysis is best performed on a homogeneous solution of low viscosity and low acidity, these techniques generally include a sample dilution step.

Dry ashing usually involves placement of the filter sample in a crucible and heating it in a muffle furnace. The temperature should be low enough to avoid loss of highly volatile analyte forms and high enough to ensure complete combustion of the filter and any organic particulates. Ashing at 500-550 $^{\circ}\text{C}$ for 4-16 hours is generally suitable. While dry ashing can be extensively used, there are some elements in some matrices for which dry ashing cannot be used because of the high volatility (lead in the presence of chlorides, for example).

Another dry ashing technique is low temperature oxygen plasma ashing. Although use of a lower temperature in a plasma ashing device prevents analyte loss due to volatility, the ashing time required may be up to 24 hours per sample.

Wet ashing procedures are extensively used and recommended by NIOSH for industrial hygiene air filter analyses by AA. Depending on the element analyzed and the AA technique employed (flame, graphite furnace, or vapor generation), various acid concentrations and mixtures may be used. In general, heating an MCE filter in a few milliliters of concentrated nitric acid completely decomposes the filter and dissolves particulate matter. Perchloric acid may also be required to oxidize certain organic substances present in the particulate matrix. A typical acid mixture is 5 mL concentrated HNO_3 with 0.5 mL 60% HClO_4 , i.e. a 10:1 ratio of nitric to perchloric. Addition of this acid may cause volatility losses. Furthermore, due to the high reactivity of perchloric acid, its use is not recommended unless absolutely necessary. However, it can be used to decompose otherwise resistant organic substances in the particulate sample, provided that proper precautions are strictly observed.

Extraction of MCE filters is recommended by NIOSH when highly volatile forms of the analyte might otherwise be lost. Selenium, for example, is typically extracted with 0.1% nitric acid.

The selection of the best filter preparation scheme for an AA analysis depends upon the element to be analyzed, the nature of the particulate matter collected on the filter, and the methods available to the analyst. Consequently, although the NIOSH recommended procedures are a good starting point, IH analysts may have to make adaptations or develop their own filter preparation methods.

Blank Corrections

MCE filters, like analytical reagents, may contain significant amounts of the analyte of interest. Consequently, to avoid errors due to contributions by the filters themselves, a filter blank must be treated and analyzed in the same way as the sample filters are. It should not, of course, be used to actually sample any air. The amount of analyte determined in the filter blank must be subtracted from that found in the samples to obtain the correct air contaminant concentrations. In the NIOSH general AA procedure for metals (96), analysis of one filter blank is recommended for every ten sample filters.

Analytical Examples

Arsenic, indium and gallium have recently been determined by furnace AA in environmental samples such as coal fly ash, plants, soils, sediments and coal. Palladium was used as a modifier for arsenic and indium, (291, 296), while nickel was chosen for gallium (294). Digestion methods were described for these samples and the modifiers not only increased the permissible ashing temperature but also enhanced the analytical signal. The Zeeman furnace technique has been applied to the determination of arsenic in pollution control samples and river sediments (292) and platinum was again used successfully as a chemical modifier.

Gallium and thallium in flue dust and city incineration waste have been determined by Zeeman furnace AA with pyrolytic platform (308, 324).

The alternate line 294.4 nm was chosen for gallium to avoid a potential spectral interference due to iron. Magnesium nitrate modifier was used.

Sulphuric acid was found useful as a volatilization suppressant for thallium. Mercury has also been determined in some environmental samples using palladium as modifier on the pyrolytic platform (325).

| Field | Environmental |
|--------------------|---|
| Sample Matrix | Atmospheric Particulates |
| Key Element | Fe |
| Also Applicable to | Al, Ca, Cd, Co, Cr, Mg, Ni, Pb, Zn |
| Reagents Required | Distilled, deionized water (DOW); high purity acids: hydrochloric acid, nitric |
| Sampling Equipment | Membrane filters: 0.05 µm and 0.1 µm pore size;* filter holder; calibrated portable air sampling pump. |

Sample Preparation

Attach the clean filter holder complete with filter to the pump inlet with plastic tubing. Obtain the sample and note the volume sampled. Return the filter canister to the laboratory.

Remove the filter with PTFE forceps and place the filter in a PTFE beaker.

Add an aliquot (10 mL) of either pure hydrochloric acid or ultrapure aqua regia to the PTFE beaker. Cover with thermoplastic, place in an ultrasonic bath and agitate for half an hour to remove the particles from the filter.

The filter is then removed and discarded. The remaining solution is analyzed by depositing the sample on the furnace.

Standard Preparation

Aqueous standards: stock standard solution 1000 µg/mL metal in 1 N acid.

Calibration Procedure

A standard addition method is used (Chapter Five).

Notes

Great care must be taken at all stages to reduce contamination arising from reagents, glassware and filtering equipment. In order to minimize the trace metal blank levels, the membrane filters should be immersed in aqua regia for half an hour, rinsed with deionized water and loaded into the filter holder while wet and allowed to dry in a vacuum desiccator. Precautions must also be taken to minimize contamination with the equipment. Clean the filter holder by immersion in dilute aqua regia. The syringe tips for dispensing the sample on to the furnace should be boiled in 5% sodium ethylenediaminetetra acetic (EDTA) acid for half an hour, rinsed with deionized distilled water and dried in a vacuum desiccator.

Clean the PTFE beakers (100 mL) by immersion in aqua regia (10%) for 24 hours, and fill with deionized distilled water to prevent further contamination before being stored.

*Various regulatory bodies stipulate a specific pore size which is necessary for compliance with the law.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Fe | | Furnace Operating Conditions | | | |
|----------------|------------|------------------------------|----------|----------|---|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 75 | 5 | 3.0 | Argon | Dry stage |
| 2 | 90 | 60 | 3.0 | Argon | 20 µL sample ensure drop dries without loss |
| 3 | 120 | 10 | 3.0 | Argon | |
| 4 | 600 | 10 | 3.0 | Argon | Ash stage, set to ensure no loss of analyte |
| 5 | 600 | 25 | 3.0 | Argon | |
| 6 | 600 | 1.5 | 0 | Argon | Gas stop |
| 7 | 2300 | 0.9 | 0 | Argon | Maximum ramp |
| 8 | 2300 | 2 | 0 | Argon | Atomize stage |
| 9 | 2300 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Other Elements

Set the Ash stage at 75% of the maximum ash temperature listed in Chapter Four. Increase the ash temperature until loss of the analyte is observed, and then reduce the temperature accordingly. Atomization temperatures are listed under their respective elements in Chapter Four.

Agriculture

Plants, Soils, Fertilizers and Feedstuffs

Trace elemental analysis of agricultural samples is important for nutritional and toxicological reasons (113). Samples include: commercial livestock feed, fertilizers, grasses, plant material, grains, forages and soils.

The elements that can be determined in agricultural samples by atomic absorption include Ag, Al, As, Au, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Mo, Mn, Na, Ni, P, Pb, Sb, Se, Si, Sr, Ti, V, Zn. Most of these elements can be easily determined by flame or hydride generation techniques as there is often no shortage of agricultural sample. Furnace atomic absorption can be used where the level of the element is not very high or the sample volume extremely small.

Generally, samples can be treated with a simple nitric acid digestion, dry ashing (temperature should not exceed 500 °C), or dilution with water - as in the case of soluble fertilizers. Many trace metal methods detailed by the A.O.A.C. (117) are generally applicable to furnace atomization which simplifies and shortens the sample pretreatment procedure for many samples.

Reference standard materials, namely the NBS orchard leaves standard (120), are recommended for the calibration of plant materials. If a standard reference material is unavailable use the method of standard additions. Plant materials, grains and fertilizers usually contain high concentrations of anions – nitrates, sulphates, phosphates, halides, etc. and cations – sodium, potassium, calcium, magnesium, etc., all of which are potential interferents. In some cases, solvent extraction may be necessary to remove the analyte from the matrix interferent (119).

A review on soils, plants and fertilizers is presented in 'Annual Reports on Analytical Atomic Spectroscopy' which should be consulted for specific references and analytical methods (see Appendix 4).

Soils

The literature contains many methods for the analysis of soils for metal content (113-118). Sampling techniques and sample treatment play important roles in the result obtained in soil analysis. The sample treatment chosen depends on the information required, time of analysis and equipment available. Methods for soil analysis have been published by the A.O.A.C. (117) and there are a number of specialist journals in which many methods using atomic absorption are published, as reviewed in reference (113).

Soil samples can be very diverse, and the following points should be considered when implementing an analysis.

- The sample must be homogeneous. This can be achieved by quartering, rolling and shaking the sample. Small portions taken from a larger spread out sample can ensure that a representative sample is analyzed.
- The metal content will depend upon the sieve used to separate fines in soil. A 200 mesh sieve usually gives higher values than an 80 mesh sieve.
- The soil sample can be treated in a variety of ways with a number of reagents depending on the form of the element required.

- In general most soil analyses are based upon air dried samples minus the 2 mm fraction. The sample is usually spread out on a clean piece of paper in a well ventilated room and covered with another piece of paper and allowed to dry for several days.
- In cases where analysis time is critical the sample can be dried in an oven at temperatures ranging from 750 °C – 105 °C. This procedure has been adequate for most metals except mercury where substantial loss has been evident.

Sample Treatment

The soil sample can be treated in a variety of ways depending on whether the analyst requires total metal, acid extractable metal or available metal.

Total Metal

The total metal in the sample is the concentration of metal after a complete and rigorous digestion.

Acid Extractable Metal

Many combinations of nitric, sulphuric, hydrochloric and perchloric acids have been used to determine acid extractable metals. Methods have varied widely depending on the information required and nature of the sample. The values obtained from acid leaching methods give an indication of the metal available to plants.

Available Metal

The available metal is a reasonable estimate of the amount of metal available to plants. This usually involves an extraction of the soil with a weak acid or chelating agent such as acetic acid or EDTA.

Analytical Examples

The Varian graphite tube atomizer has been successfully applied to the determination of trace molybdenum in plant tissues after a solvent extraction step into di-isobutyl ketone (326). Initial digestion was carried out in a mixture of sulphuric, nitric and perchloric acids. Excellent correlation was reported for NBS Standards.

M. Hoenig et al have studied the factors which influence the measurement of molybdenum in plant samples by GTA-95 (327). They found that an integration method (peak area) was preferred and confirmed that a nitric acid hydrogen peroxide digestion was entirely suitable.

The use of ascorbic acid as a modifier for several metals in plant samples by the platform technique has also been shown by Hoenig et al (328). Metals determined were lead, antimony, thallium, nickel, chromium and cadmium, while several sample types were examined. Arsenic has been measured in acid digested soil samples using palladium modifier (291).

| Field | Agriculture |
|------------------------|--|
| Sample Matrix | Soil: Total metal, acid extractable metal, available metal |
| Key Element | Cu |
| Also Applicable to | Most trace elements |
| Reagents Required | |
| Total metal | Concentrated perchloric acid Concentrated hydrofluoric acid |
| Acid extractable metal | Concentrated hydrochloric acid |
| Available metal | Glacial acetic acid |

Sample Preparation

Total Metal

Weigh 0.1 g of soil into a platinum crucible wetted with water and digest with 0.5 mL 72% perchloric acid and 5 mL of 48% hydrofluoric acid on a sand bath at 200 – 225 °C, ensuring the crucible is partially covered with a platinum lid and the sample is not taken to dryness. The residue is taken up by boiling the sample with 5 mL of 60% hydrochloric acid (6N) and 10-15 mL of water. The contents of the crucible are transferred to a 100 mL volumetric flask with washing of the crucible and lid. Depending on the sample, further additions of the reagents may be required to complete the digestion.

Acid Extractable

Weigh out 10 g of air dried sample and shake with 20 mL of 1 N HCl for 18 hours at room temperature. Centrifuge the treated sample, filter the supernatant into a volumetric flask and make up with water for analysis.

Available Metal

Weigh out 2 g of air dried soil into a polyethylene bottle. Add 40 mL of 2.5% acetic acid and shake for 12 hours. Filter the treated sample into a volumetric flask using a Whatman 540 paper and make up with water for analysis.

Standard Preparation

Aqueous Standards: Standard stock solution 1000 µg/mL Cu in 1 N HCl.

Chemical Modifier

For copper, if excessive sodium chloride is present in the sample, 40 µL of ammonium nitrate (1% solution) can be added to a 20 µL sample.

Calibration Procedure

Normal calibration against three standards of the element of interest in the same acid as the sample. If matrix interferences are present then a standard additions method is recommended.

Notes

Total metal, acid extractable metal and available metal procedures will vary depending on the reference consulted and nature of sample.

Cadmium will be lost from a 5% HCl sample at 400 °C.

Ammonium dihydrogen phosphate (1% - 2%) or phosphoric acid (3%) can be used as a chemical modifier for cadmium which allows an ash of 600 °C.

Typically 40 µL of chemical modifier is added to 20 µL of sample.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cu | | Furnace Operating Conditions | | | |
|----------------|------------|------------------------------|----------|----------|---|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 75 | 5 | 3.0 | Argon | Dry stage |
| 2 | 90 | 60 | 3.0 | Argon | 20 µL sample ensure drop dries without loss |
| 3 | 120 | 10 | 3.0 | Argon | |
| 4 | 600 | 10 | 3.0 | Argon | Ash stage, set to ensure no loss of analyte |
| 5 | 600 | 25 | 3.0 | Argon | |
| 6 | 600 | 1.5 | 0 | Argon | Gas stop |
| 7 | 2300 | 0.9 | 0 | Argon | Maximum ramp |
| 8 | 2300 | 2 | 0 | Argon | Atomize stage |
| 9 | 2300 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Check to ensure the drop dries appropriately and does not splutter.

Other Elements

Metal chloride salts are usually more volatile than their oxy anion analogs and, as a result, require lower ash temperatures. For metals in hydrochloric acid, set the ash stage at 75% of the maximum ash temperature recommended in Chapter Four.

| Field | Agriculture |
|--------------------|-------------------|
| Sample Matrix | Plant tissue |
| Key Element | Ni |
| Also Applicable to | Mo, Pb, Cd |
| Reagents Required | Nitric Acid (70%) |

Sample Preparation

Accurately weigh 2.0 g of dried plant material into 250 mL conical flasks. Add 20.0 mL of 7N nitric acid (50%). Boil mixture on a hot plate for 20 minutes. Cool and filter (Whatman No. 30) into 100 mL volumetric flasks. Dilute to volume with distilled water.

Calibration Procedure

Aqueous standards: stock standard solution 1000 µg/mL Ni in 1N HCl. Working standards should contain nitric acid (5%). Check method using NBS orchard leaves (NBS No. 1571).

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Ni | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 75 | 5 | 3.0 | Argon | Dry stage 20 µL sample |
| 2 | 90 | 60 | 3.0 | Argon | |
| 3 | 120 | 10 | 3.0 | Argon | Ash stage |
| 4 | 700 | 15 | 3.0 | Argon | |
| 5 | 700 | 30 | 3.0 | Argon | Gas stop |
| 6 | 700 | 2 | 0 | Argon | |
| 7 | 2400 | 0.9 | 0 | Argon | Atomize stage |
| 8 | 2400 | 2 | 0 | Argon | |
| 9 | 2400 | 1 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Check dry stage parameter to ensure even drying and no spluttering occurs on progression to the ash stage.

Other Elements

For molybdenum and lead, set the respective recommended maximum ash and atomize conditions listed in Chapter Four.

For cadmium, H₃P₀4 (2%) or ammonium dihydrogen phosphate (2%) may be used as modifiers, allowing a maximum ash setting of 600 °C. The chemical modifier (40 µL) can be added to the sample (20 µL prior to starting the program. Check the modifiers for purity and set the dry stage (step 2) to accommodate a 60 µL volume (increase the time accordingly).

| Field | Agriculture |
|---|-------------------------------|
| Sample Matrix | Feed grains and forages (119) |
| Key Element | Co |
| Reagents Required | |
| (a) 1-nitroso-2-naphthol solution. Dissolve 2.5 g of 1-nitroso-2-naphthol in 125 mL of acetic acid and dilute to 250 mL with water. | |
| (b) Sodium citrate solution. Dissolve 500 g of dehydrated sodium citrate in water and dilute to about 900 mL. Adjust to pH 7 with citric acid and dilute to 1 L with water. | |

Sample Preparation

Accurately weigh 2-3 g of material into a vycor crucible and ash at 450 °C in a muffle furnace for 6 hours. Cool, add 40 mL of 1:3 HCl and 3 or 4 drops of HNO₃. Heat slowly for 2-3 hours, evaporating volume to 5-10 mL. Transfer solution to a 150 mL beaker with 50 mL water. Adjust pH to 3-4 with sodium citrate solution.

Extraction Procedure

Transfer to a separatory funnel and add 5 mL of 1-nitroso-naphthol solution and mix well. Let stand 1 hour with occasional shaking. Extract two times with 10 mL CHCl₃ by shaking vigorously for several minutes. Combine and gently evaporate to near dryness. Dilute to 5 mL with CHCl₃. Extract 25mL standards with 25 mL CHCl₃, and dilute to 25 mL CHCl₃.

Standard Preparation

Aqueous standard: stock standard solution 1000 µg/mL Co in HCl. Prepare aqueous standards containing 0.02, 0.05 and 0.1 µg/mL Co.

Calibration Procedure

Normal calibration against three extracted standards.

Notes

The extraction procedure eliminates the interference from Fe, Mn and Mg encountered with direct analysis. Stopper the extracted sample to ensure no evaporation occurs.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Co | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 40 | 10 | 1.0 | Argon | Dry stage maximum volume 20 µL sample |
| 2 | 60 | 30 | 3.0 | Argon | |
| 3 | 600 | 5 | 3.0 | Argon | Ash stage |
| 4 | 600 | 30 | 3.0 | Argon | |
| 5 | 600 | 2 | 0 | Argon | Gas stop |
| 6 | 2300 | 1.8 | 0 | Argon | Atomize stage |
| 7 | 2300 | 2 | 0 | Argon | |
| 8 | 2300 | 1 | 3.0 | Argon | Tube clean |

Read Command: Steps 6 to 7

Ramp Step: 6. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Chloroform is extremely volatile (boiling point about 60 °C), and the setting of the dry stage is extremely important. A lower temperature may be required to facilitate smooth drying. Injection of the sample on to a warm tube (50 °C) has also been used to prevent spillage from the graphite tube plateau. The ramp rate given above is approximately 1000 °C/s. The sensitivity for most elements is usually poorer with a reduced ramp rate.

| Field | Agriculture |
|--------------------|--------------------|
| Sample Matrix | Urea pellets (119) |
| Key Element | Cr |
| Also Applicable to | Mo and Te |

Sample Preparation

Accurately weigh 2 g of sample and dissolve in distilled water. Dilute to 25 mL and inject directly.

Standard Preparation

Aqueous standards: Stock standard solution 1000 µg/mL Cr in 1 N HCl.

Calibration Procedure

Normal calibration against three standards over the range of sample response.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cr | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 75 | 5 | 3.0 | Argon | Dry stage 20 µL sample |
| 2 | 90 | 60 | 3.0 | Argon | |
| 3 | 120 | 10 | 3.0 | Argon | Ash stage |
| 4 | 700 | 5 | 3.0 | Argon | |
| 5 | 700 | 40 | 3.0 | Argon | Gas stop |
| 6 | 700 | 2 | 0 | Argon | |
| 7 | 2500 | 0.9 | 0 | Argon | Atomize stage |
| 8 | 2500 | 2 | 0 | Argon | |
| 9 | 2500 | 1 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

If the ash and atomization peaks substantially overlap, reduce the ramp rate. A reduced ramp rate may reduce sensitivity. Most of the urea can be ashed off at 600 °C and should not interfere with the atomize signal.

Other Elements

For iron and molybdenum set the ash stage (steps 4-6) at 75% of recommended maximum ash temperatures and the atomize stage (steps 7-8) at the recommended values listed in Chapter Four.

| Field | Agriculture |
|-------------------|---|
| Sample Matrix | Commercial livestock feed (119) |
| Key Element | Mo |
| Reagents Required | 8-hydroxy-quinoline, 4% soln. - Dissolve 8 g of reagent grade 8-hydroxy-quinoline in 200 mL distilled water. Adjust pH to 0.85 with 50% sulphuric acid. |

Sample Preparation

Accurately weigh 10 g of sample into a porcelain crucible and ash in a muffle furnace at 450 °C for 6 hours. Cool and dissolve the ash in 1:3 HCl (about 20 mL). Adjust the pH to 1 with dilute NaOH. Transfer to an appropriate separatory funnel. Add 10 mL to the 4%, 8-hydroxy-quinoline solution. Add 10 mL of Chloroform (CHCl₃) and shake vigorously for several minutes. Dilute or evaporate CHCl₃ sample solution to contain between 0.05 and 0.2 µg/g Mo.

Standard Preparation

Aqueous standards: Standard stock solution 1000 µg/mL Mo in 2% hydrochloric acid. Prepare standards containing 0.05, 0.1, 0.2 µg/mL Mo. Working standards are prepared by pipetting to mL of each standard into separatory funnel. Add 10 mL of the 4% 8-hydroxy-quinoline. Add 100 mL of CHCl₃ and shake vigorously for several minutes.

Calibration Procedure

Normal calibration on extracted standards.

Notes

Some interferences have been noted if analyses on the acid solution are carried out directly. Solvent extraction alleviates these effects.

This method can also be applied to the analysis of forages, and commercial fertilizers.

Stopper vessels containing extracted samples to prevent evaporation.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Mo | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|-----------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 40 | 10 | 1.0 | Argon | Dry stage |
| 2 | 60 | 30 | 3.0 | Argon | maximum volume 20 µL sample |
| 3 | 700 | 10 | 3.0 | Argon | Ash stage |
| 4 | 700 | 30 | 3.0 | Argon | |
| 5 | 700 | 2 | 0 | Argon | Gas stop |
| 6 | 2600 | 1 | 0 | Argon | Atomize stage |
| 7 | 2600 | 2 | 0 | Argon | |
| 8 | 2600 | 1 | 3.0 | Argon | Tube clean |

Read Command: Steps 6 to 7

Ramp Step: 6. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Chloroform boils at about 60 °C and is extremely volatile; the setting of the dry stage is extremely important. Injection during the dry stage on a hot tube has been achieved using chloroform. However, the maximum volume dispensable with a tube at ambient temperature is 20 µL for CHCl₃.

Biological and Biochemical

Analysis of biological samples is an important application of graphite tube atomization. The advantages in terms of analytical sensitivity and ability to analyze very small sample volumes are often of major importance in selecting the technique.

Blood, Serum and Urine

In modern medicine, trace elements are receiving considerable attention as the two extremes of great excess and gross deficiency continue to be recognized. The measurement of very low concentrations of trace metals, often on volumes less than 1 mL, has presented a considerable challenge to the analytical chemist. In many instances graphite tube atomization has permitted rapid and precise analysis of such samples.

There are a number of trace elements which are regarded as performing functions essential to life. Table 8 contains a list of such elements together with some typical levels found in man (121-123). There is considerable debate about what is regarded as a 'normal' level for many elements, and values reported for some elements can vary considerably (123).

Table 8. Normal concentrations of essential trace elements in blood and urine

| Element | Serum Mean µg/L | Blood Mean µg/L | Urine Mean µg/L |
|------------|--------------------|--------------------|--------------------|
| Chromium | 0.5 | 0.5 | 10 |
| Manganese | 0.5 | 5.0 | 300 |
| Iron | 1200 | | 180 |
| Cobalt | 0.2 | 2.0 | 100 |
| Copper | 1100 | 1200 | 60 |
| Zinc | 1000 | | 900 |
| Molybdenum | 1.0 | 100 | 100 |
| Selenium | 100 | 150 | 30 |
| Strontium | 50 | | 150 |
| Nickel | 5.0 | 5.0 | 85 |
| Vanadium | 0.5 | 4.0 | 16 |

In contrast to those essential elements, there are several metals which are regarded as toxic. Their widespread use in industry has sometimes meant that their levels in the environment have increased.

Table 9 shows levels of toxic of abnormal elements found in man. Reported values can vary significantly from those quoted (123).

Table 9. Concentrations of toxic abnormal trace elements found in blood and urine

| Element | Blood Mean µg/L | Urine Mean µg/L |
|-----------|--------------------|--------------------|
| Cadmium | 3.0 | 12 |
| Lead | 200 | 40 |
| Mercury | 3.0 | 10 |
| Antimony | 20 | 0.05 |
| Tin | 3.0 | 0.02 |
| Arsenic | 2.0 | 50 |
| Barium | 2.0 | 0.02 |
| Beryllium | 0.4 | 1.0 |
| Lithium | 3.0 | 500 |

Graphite furnace atomization has had widespread application in the analysis of trace metals in biological fluids and in body tissues.

Analytical procedures for flame and graphite furnace AA analysis of nineteen elements in biological fluids and tissues have been summarized (122). Another monograph reviews all fields of analytical interest and provides a summary of procedures used (124). Trace elements in serum are often analyzed directly but the serum may also be diluted for some elements which are present at higher levels. Diluents can range from 5% trichloroacetic acid (TCA) solutions to a dilute (1%) Triton X-100 solution.

Difficulty has generally been experienced in directly analyzing whole blood, largely because of the frothing which occurs during the drying stage. Whole blood is also difficult to dispense accurately and most analytical methods involve a dilution (typically 1:1) with another reagent. For most trace elements, greater dilutions are not practicable, but some elements may be present at levels which permit greater dilutions. Reagents which have been used include concentrated nitric acid with digestion at about 85 °C for 20 minutes (125) and 1-5% aqueous Triton X-100 solution followed by thorough vortexing (126). Antifoam agents have also assisted in blood analysis.

There are a multitude of analytical methods for metals in biological samples. Those furnace AA techniques which have involved Varian Carbon Rod Atomizers were reviewed (127). Cobalt in blood and serum has been analyzed following an extraction procedure into chloroform (128). The biological field represents one of the most demanding applications in furnace AA.

Background absorption is often present and it is therefore necessary to use a background corrector for most elements. Reagents for sample treatment and the program parameters are chosen to minimize the background absorption (125).

Samples themselves contain high concentrations of matrix materials and it is often necessary to prepare standards which are carefully matched to the samples. Simple aqueous standards can rarely be used; the standard additions technique is generally adopted (see Chapters Five and Six).

The measurement of aluminum in blood serum is important for dialysis patients. A method has been reported in which the serum is diluted (1 + 2) with distilled water prior to the analysis. Ashing took place at up to 1400 °C and aqueous standards were found to be adequate (129). A similar method for aluminum in serum employs dilution with a Triton X-100 solution and a standard additions technique (127).

Low levels of selenium in serum have been measured using nickel as a stabilizer and a standard additions technique for calibration (30).

A recent study examined the background signals obtained from various biological samples (329). It was revealed that the addition of about 25% nitric acid considerably reduced the background signal. Oxygen ashing was also beneficial.

Tissues

Before tissues are analyzed, the sample is usually dried to permit accurate weighing. The tissue sample is not normally analyzed directly, but digested in suitable acids prior to introduction into the graphite furnace. Several digestion procedures are commonly used involving HNO_3 and H_2SO_4 , H_2SO_4 and H_2O_2 , or HNO_3 above (124, 127). Sulphuric acid is not recommended for lead analysis. Care should be taken if HCl is used because poor recoveries may result for some of the volatile elements when heated in this matrix.

Confirmation of the accuracy of the method with a standard reference material (e.g. NBS bovine liver) is recommended. Normally the method of standard additions would be required in order to maintain accuracy. Simple aqueous solutions are rarely acceptable to establish the analytical curve, because of the interference of the matrix on the analytical signal. If approximate answers only are required, aqueous solutions would be suitable for calibration.

Some methods involve the analysis of wet tissue which is homogenized and digested with selected reagents. In this case the moisture content should be known to maintain the accuracy of the analysis.

Other Biological and Biochemical Samples

Graphite furnace atomization has been employed for the analysis of a wide variety of biological samples. Digestion procedures depend on sample type and may involve wet digestion methods (72, 73) or decomposition in a sealed PTFE vessel (131). Interference effects in biological samples, for the analysis of copper and manganese, have been reported (132).

The analysis of ruthenium which was used as a solid-phase marker in the digestion of ruminants has been successful (133). A novel application was for the analysis of drosophila (fruit fly) for Cd, Cu and Pb. Digestion was completed in HNO_3 and H_2O_2 (134).

Fish and clam tissue have been analyzed for lead and cadmium following a suitable digestion procedure (135).

Recent Analytical Examples

The Varian GTA-95 has been successfully used for aluminum and manganese in serum, lead in blood, and chromium in urine (330), and for cadmium in blood (304). The platform was used for cadmium determination and nitric acid was added as a modifier.

There has been considerable discussion about the measurement of selenium in serum, due to spectral interferences from iron and phosphate (331-335). However, a GTA-95 with pyrolytic platform has been successfully applied to selenium in blood and urine samples after careful selection of operating parameters (336).

The difficulty experienced with the deuterium background correction system is the spectral interference due to high concentrations of iron and close proximity of an iron line to the selenium line. An over correction usually results with the deuterium arc system, but there is no such problem with the Zeeman graphite furnace atomizer. The deuterium arc background correction system can only be used successfully for the determination of selenium in whole blood when special operating conditions apply, including the use of a nickel modifier (336).

Many other workers have been unable to measure selenium in whole blood (due to iron spectral interference with the deuterium arc system), but have measured selenium in blood plasma (337). The Zeeman system is the preferred choice for this analysis and some examples have been given (338).

Extensive studies on the measurement of gallium in biological samples have been reported and EDTA was successful in suppressing some interferences (339).

Aluminum remains an important element with respect to haemodialysis patients and a recent paper discusses its measurement in serum, blood, urine and tissue. Dilution with Triton X-100 was favored and precautions in avoiding contamination were discussed (340).

Pybus has recently studied the measurement of aluminum in serum and dialysate and has developed methodology for the GTA (341).

The benefits of oxygen ashing together with selected modifiers have been described for the determination of lead in blood (367). Blood was simply diluted with a Triton X-100 solution and an oxygen ash at 900 °C reduced the background signal without loss of lead.

In recent years, Zeeman furnace AA has been applied to many biological sample types. The following literature references all use this technique.

Arsenic has been measured in blood serum with nickel as modifier (342) while chromium has been determined in whole blood and serum after dilution with Triton X-100 (312). With chromium, air ashing facilitated the analysis.

For cadmium and lead in blood, samples were analyzed on a pyrolytic platform after dilution in Triton X-100 (343). A standard additions calibration procedure was required. In other work lead in blood was determined from the platform using a modifier of ammonium dihydrogen phosphate and magnesium nitrate (344).

Urinary lead was measured after stabilizing the sample in nitric acid, by the pyrolytic platform technique. Ammonium dihydrogen phosphate modifier was also required (345).

| Field | Biological |
|-------------------|---|
| Sample Matrix | Whole Blood |
| Key Element | Cd |
| Reagents Required | Ammonium pyrrolidine dithiocarbonate (APDC) Methylisobutylketone (MIBK) Dilute hydrochloric acid Ammonium dihydrogen phosphate Triton X-100 Antifoam-B (Dow Corning) |

Sample Preparation

Blood Samples

Prepare a dilution solution of 0.2% Triton X-100 with 0.2% Antifoam-B. Combine equal volumes of whole blood and Triton X-100/Antifoam-B solution in a centrifuge tube. Vortex vigorously for 30 seconds to produce complete lysis of the cellular elements of the blood. Centrifuge the samples and analyze the clear supernatant.

Ammonium dihydrogen phosphate Clean Up — Removal of Cd Contamination

Prepare a solution of 2 g of ammonium dihydrogen phosphate in 100 mL of deionized distilled water. Adjust the pH of the solution to between 1 and 6 with dilute hydrochloric acid.

Prepare a 1% APDC solution in deionized distilled water. This reagent should be prepared fresh daily.

Mix 5 mL of the APDC solution with the 100 mL of ammonium dihydrogen phosphate solution. Shake the solution for two minutes with 10 mL of MIBK in a separating funnel. Withdraw the aqueous layer and discard the organic layer. The extraction process is repeated twice more. The extracted modifier is then stored in a clean polyethylene container.

Standard Preparation

Prepare a 3 ng/mL aqueous cadmium nitrate standard in 1% nitric acid from a suitable stock solution.

Calibration Procedure

Use the standard additions method of calibration and employ the programmable sample dispenser to assemble the additions. To a 5 µL sample volume add 2 and 4 µL of the standard. Combine this with 10 µL of the extracted ammonium dihydrogen phosphate modifier.

Notes

All reagents should be tested for Cd contamination. The Antifoam-S reagent aids in dispensing, but Triton X-100 alone should also be satisfactory.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cd | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|-----------------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 40 | 3.0 | Argon | |
| 3 | 140 | 20 | 3.0 | Argon | |
| 4 | 300 | 10 | 3.0 | Argon | |
| 5 | 450 | 5 | 0.1 | Oxygen | Oxygen |
| 6 | 450 | 5 | 0.1 | Oxygen | ashing stage Note low gas flow |
| 7 | 650 | 10 | 3.0 | Argon | Argon ashing stage |
| 8 | 650 | 10 | 3.0 | Argon | |
| 9 | 650 | 1 | 0 | Argon | Gas stop |
| 10 | 2500 | 1 | 0 | Argon | Atomize stage |
| 11 | 2500 | 1 | 3.0 | Argon | |

Read Command: Steps 10 to 11

Ramp Step: 10. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Oxygen ashing is used in the furnace program. Low oxygen flow and a maximum oxygen ash temperature of 450 °C are used to minimize tube wear.

| Field | Biological |
|-------------------|---|
| Sample Matrix | Whole Blood |
| Key Element | Pb |
| Reagents Required | Aqueous solution of 0.2% Triton X-100 with 0.2% Dow Corning Antifoam-B. |

Sample Preparation

Mix one volume of whole blood with an equal volume of the Triton X-100/Antifoam-B solution in a centrifuge tube and vortex for about thirty seconds. This rapidly produces lysis of cellular elements in the blood. Centrifuge the mixture and analyze the supernatant clear liquid.

Standard Preparation

Prepare a 100 µg/L lead standard in 1% nitric acid from a suitable lead stock solution.

Calibration Procedure

Use the standard additions technique and employ the programmable sample dispenser to assemble the additions. At least two additions are necessary. Additions of 2 and 4 µL of the standard to a 10 µL volume of blood should be satisfactory.

Notes

A lower signal is obtained for lead in blood compared with aqueous solutions and the standard additions technique is therefore necessary to obtain accurate results. Some ash build up may occur in the graphite tube after many samples have been analyzed. Sample volumes of 5 µL may be used for normal levels. The Antifoam-B reagent aids in sample dispensing, therefore improving precision.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Pb | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 40 | 3.0 | Argon | |
| 3 | 120 | 20 | 3.0 | Argon | |
| 4 | 300 | 8 | 3.0 | Argon | Start of ash |
| 5 | 450 | 7 | 0.5 | Air | Air facilitates ashing |
| 6 | 480 | 8 | 0.5 | Air | |
| 7 | 480 | 5 | 3.0 | Argon | Argon purge after air ash |
| 8 | 480 | 2 | 0 | Argon | Gas stop |
| 9 | 2600 | 1.1 | 0 | Argon | Atomize stage |
| 10 | 2600 | 1 | 0 | Argon | |
| 11 | 2600 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 8 to 10

Ramp Step: 9. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

The 283.3 nm wavelength is preferred over the 217.0 nm line with the Zeeman furnace.

Other Elements

The method is suitable for other elements in whole blood. The standard additions method of calibration should be used. The air ashing temperature should not exceed 480 °C to minimize tube wear.

| Field | Biological |
|-------------------|--|
| Sample Matrix | Whole Blood |
| Key Element | Se |
| Reagents Required | Diluting agent consisting of 0.5% Triton X-100. 0.125% Dow Corning Antifoam-8, and 0.25% ascorbic acid. 0.05% Pd solution as modifier. |

Sample Preparation

Vortex the blood sample. Add 0.5 mL of the whole blood to 2 mL of the diluting agent and vortex vigorously.

Standard Preparation

Prepare a 100 µg/L solution of Se in 1% hydrochloric acid from high purity salts or stock standard solutions in hydrochloric acid.

Calibration Procedure

Use the standard additions technique. Aliquots of 5 and 10 µL of standard are added to the sample. Sample volumes as high as 20 µL can be used. 10 µL of the Pd modifier are used. The modifier is pre-injected using the programmable sample dispenser.

Notes

The presence of oxidizing agents such as nitric acid in the modifier or standard must be avoided. The method relies upon the reduction of the Pd modifier by the ascorbic acid. Air or oxygen ashing cannot be introduced prior to atomization. A burn out step at 400 °C with air can be used after atomization, ie, a cool down step, to reduce carbon build-up.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Pb | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 80 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 60 | 3.0 | Argon | |
| 3 | 300 | 20 | 3.0 | Argon | |
| 4 | 1200 | 10 | 3.0 | Argon | Ash stage |
| 5 | 1200 | 15 | 3.0 | Argon | |
| 6 | 1200 | 1 | 0 | Argon | |
| 7 | 2700 | 0.8 | 0 | Argon | Atomize stage |
| 8 | 2700 | 1 | 0 | Argon | |
| 9 | 2700 | 2 | 3.0 | Argon | |
| 10 | 400 | 0 | 3.0 | Argon | |
| 11 | 400 | 5 | 3.0 | Air | Carbon burn out |
| 12 | 80 | 0 | 3.0 | Argon | Argon purges air |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

| Field | Biological |
|-------------------|---|
| Sample Matrix | Whole Blood |
| Key Element | Al |
| Reagents Required | Aqueous solution of 0.2% Triton X-100 with 0.2% Dow Corning Antifoam-B. |

Sample Preparation

One volume of serum is added to an equal volume of the Triton X-100/Antifoam-B solution. Vortex for thirty seconds.

Standard Preparation

Prepare a 10 µg/L aluminum standard in 1% nitric acid from a suitable lead stock solution.

Calibration Procedure

The standard additions method of calibration is used. At least two additions are necessary. Aliquots of 5 and 10 µL of the standard may be added to 10 µL of sample using the programmable sample dispenser.

Notes

The Antifoam-B reagent aids in sample dispensing, therefore improving precision.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Al | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 35 | 3.0 | Argon | |
| 3 | 120 | 10 | 3.0 | Argon | |
| 4 | 1100 | 20 | 3.0 | Argon | Ashing stage |
| 5 | 1100 | 10 | 3.0 | Argon | |
| 6 | 1100 | 2 | 0 | Argon | Gas stop |
| 7 | 2500 | 0.7 | 0 | Argon | Atomize stage |
| 8 | 2500 | 1 | 0 | Argon | |
| 9 | 2500 | 1 | 3.0 | Argon | |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Under the conditions used the background signal was minimal. Argon improves the atomic signal by about a factor of two compared with nitrogen. Normal levels of Al in serum are about 10 µg/L and care must be taken to avoid contamination.

| Field | Biological |
|-------------------|---|
| Sample Matrix | Whole Blood |
| Key Element | Mn |
| Reagents Required | Aqueous solution of 0.5% Triton X-100 with 0.5% Dow Corning Antifoam-B. |

Sample Preparation

Four volumes of blood serum are mixed with one volume of the Triton X-100/Antifoam-B solution. Vortex for 30 seconds.

Standard Preparation

Prepare a to 10 µg/L manganese standard solution in 1% nitric acid from a suitable stock solution.

Calibration Procedure

Use the standard additions method of calibration. To a 10 µL sample add 2 and 4 µL additions of the standard using the programmable sample dispenser.

Notes

The standard additions method of calibration is necessary to establish an accurate calibration.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Mn | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|--------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 40 | 3.0 | Argon | |
| 3 | 120 | 20 | 3.0 | Argon | |
| 4 | 300 | 5 | 3.0 | Argon | Start of ash stage |
| 5 | 400 | 20 | 3.0 | Argon | |
| 6 | 1100 | 5 | 3.0 | Argon | High |
| 7 | 1100 | 10 | 3.0 | Argon | temperature ashing |
| 8 | 1100 | 2 | 0 | Argon | Gas stop |
| 9 | 2500 | 0.7 | 0 | Argon | Atomize stage |
| 10 | 2500 | 1 | 0 | Argon | |
| 11 | 2500 | 1 | 3.0 | Argon | Tube clean |

Read Command: Steps 9 to 10

Ramp Step: 9. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

Negligible background absorption was detected during atomization under the conditions used. Normal levels of manganese in serum are quite low at about 2 µg/L and care must be taken to avoid contamination. Higher sample volumes with appropriately increased drying times could be used to increase the signal for lower levels of manganese.

Foods and Beverages

While it is possible to measure a number of elements in foods, juices and beverages directly by flame AA because of their high levels, it is often necessary to use graphite furnace AA to detect low levels. The widespread use of metals in modern industrial processes had led to traces of many toxic or undesirable metals in our environment. Legislation in most countries requires that food and drinks contain less than specified amounts of certain toxic metals.

Graphite furnace AA is of significant benefit in detecting trace elements in foods and drinks. A Varian GTA-96 has been applied to the measurement of lead in infant milk formula and in fish digests (298). The milk was analyzed after dilution with Triton X-100 and ammonium dihydrogen phosphate was used as modifier. Although the milk was analyzed directly on the graphite tube, it was necessary to use the pyrolytic platform for the analysis of the fish digest. In both cases the automated standard additions procedure was applied.

Various palm oil samples have been analyzed for copper, nickel, lead and iron by graphite furnace AA. Palm oil samples were simply diluted in di-isobutylketone and calibration established from suitable organometallic standards (346). Guidance was provided in establishing the optimum furnace parameters and in selecting the preferred automated standard additions calibrations procedure.

A collaborative study was recently undertaken on the measurement of lead in infant milk formulas by furnace AA (347). Samples were typically digested in nitric acid and a modifier mixture (citric acid, hydrogen peroxide and ammonium dihydrogen phosphate) was added.

A combination of modifier, pyrolytic platform and maximum temperature ramp were found to be desirable for the determination of lead in fish tissues (348). Once again the modifier chosen for lead was a solution of ammonium dihydrogen phosphate.

A Zeeman graphite furnace has been applied to the measurement of lead in powdered milk and formulas without sample digestion (297). The procedure was simple and found to be accurate. In another study, results were reported on the platform determination of lead and cadmium in milk products in which oxygen ashing was used (349).

| Field | Food |
|-------------------|--|
| Sample Matrix | Fish digests |
| Key Element | Pb |
| Reagents Required | Acid digest mixture of HNO ₃ :HClO ₄ solution (6:1). De-ionized distilled water. |

Sample Preparation

Slowly digest in a conical flask with heating the wet tissue (1 g, fat free) using the digestion mixture (5 mL). Heat to 150 °C to continue digestion. Further heat to 220 °C to yield moist crystals and to remove most of the perchloric acid. Dissolve the crystals in a minimum volume of 10% HNO₃ and make up to 2 mL final volume with water (298). Observe correct safety procedures when using perchloric acid.

Standard Preparation

Aqueous standards: Standard stock 1000 mg Pb/L in 1 M nitric acid. Prepare 10 µg Pb/L standard.

Calibration Procedure

Use a pyrolytic platform and calibrate by standard additions technique. Suggested working volume is 2 µL sample with 5 and 10 µL standard additions and blank to maintain a total of 12 µL for all solutions dispensed.

Notes

The total volume should be kept to less than 20 µL.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Pb | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|----------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 150 | 5 | 3.0 | Argon | Dry stage |
| 2 | 210 | 50 | 3.0 | Argon | 20 µL maximum total volume |
| 3 | 260 | 10 | 3.0 | Argon | |
| 4 | 600 | 15 | 3.0 | Argon | Ash stage |
| 5 | 600 | 2 | 0 | Argon | Gas stop |
| 6 | 2500 | 1.5 | 0 | Argon | Atomize stage |
| 7 | 2500 | 1 | 0 | Argon | |
| 8 | 2500 | 2 | 3.0 | Argon | Tube clean |
| 9 | 40 | 12.3 | 3.0 | Argon | Cool down step |

Read Command: Steps 6 to 7

Ramp Step: 6. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

The use of a pyrolytic platform is required to reduce background. A reduced slit height is recommended. The ash temperature should not be more than 800 °C to prevent loss of analyte.

| Field | Food |
|--------------------|---|
| Sample Matrix | Infant formula, skim milk powder |
| Key Element | Pb |
| Also Applicable to | Cd |
| Reagents Required | Ammonium dihydrogen phosphate, 0.5% w/v solution (used to chemically modify the analyte). Trace metal impurities in the modifier may be removed by APDC chelation and MIBK extraction. (See notes for Sea Water Analysis.) Deionized distilled water. |

Sample Preparation

Dissolve milk powder (1.25 g) in deionized distilled water (25 mL) with vigorous agitation using a vortex mixer or ultrasonic bath. Some Triton X-100 0.01 v/v (1 mL) may be added to give better dispensing properties (298).

Standard Preparation

Aqueous standards: Standard stock 1000 µg Pb/L in 1 M nitric acid. Prepare 10 µg Pb/L standard.

Calibration Procedure

By standard additions technique using the programmable sample dispenser. Suggested volumes are 10 µL sample, 5 and 10 µL standard addition volumes, 10 µL modifier and blank to maintain a total of 30 µL for all solutions dispensed.

Notes

This method is not recommended for fresh milk or full cream milk powders. Either do an acid digest or use an oxygen ash for such samples.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Pb | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|----------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 90 | 5 | 3.0 | Argon | Dry stage |
| 2 | 100 | 65 | 3.0 | Argon | 30 µL maximum total volume |
| 3 | 125 | 25 | 3.0 | Argon | |
| 4 | 650 | 20 | 3.0 | Argon | Ash stage |
| 5 | 650 | 2 | 0 | Argon | Gas stop |
| 6 | 2500 | 1.2 | 0 | Argon | Atomize stage |
| 7 | 2500 | 1 | 0 | Argon | |
| 8 | 2500 | 2.2 | 3.0 | Argon | Tube clean |

Read Command: Steps 6 to 7

Ramp Step: 6. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

The ashing temperature should not be less than 600 °C to minimize background and not more than 950 °C to prevent loss of analyte.

Other Elements

As cadmium tends to be present in smaller amounts, the standard solution should be 5 µg Cd/L or less. For cadmium, the ash temperature should not be more than 750 °C.

| Field | Food |
|--------------------|---------------------------------|
| Sample Matrix | Palm Oil |
| Key Element | Ni |
| Also Applicable to | Fe, Cu |
| Reagents Required | 2,6-Dimethylheptan-4-one (DIBK) |

Sample Preparation

Weigh palm oil (1 g) into a 5 mL volumetric flask. Dissolve in DIBK and make up to the mark. Using an infrared lamp to melt the sample facilitates weighing and a warm ultrasonic bath facilitates dissolution. (346)

Standard Preparation

Organometallic standard supplied in a base oil and diluted in DIBK to give a working concentration of 60 µg Ni/L

Calibration Procedure

By standard additions technique. A sample volume of 5 µL is recommended. The sample is spiked with 2 and 4 µL of standard. DIBK blank is added to give a constant total volume.

Notes

Total dispensed volume should not exceed 15 µL. If an autosampler is used, the rinse solution can be an aqueous mixture of Triton X-100 (0.01% v/v) and nitric acid (0.1% v/v, 0.02 M).

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Ni | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|--------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 80 | 5 | 3.0 | Argon | Dry stage |
| 2 | 150 | 30 | 3.0 | Argon | 15 µL total volume |
| 3 | 180 | 20 | 3.0 | Argon | |
| 4 | 180 | 10 | 3.0 | Argon | |
| 5 | 800 | 10 | 3.0 | Argon | Ash stage |
| 6 | 800 | 10 | 3.0 | Argon | |
| 7 | 800 | 2 | 0 | Argon | Gas stop |
| 8 | 2400 | 0.8 | 0 | Argon | Atomize stage |
| 9 | 2400 | 2 | 0 | Argon | |
| 10 | 2400 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 8 to 9

Ramp Step: 8. Enter 0 for Maximum Ramp (2000 °C/s)

Other Elements

For iron and copper use an ash temperature of 700 °C. The copper standard can be 40 µg Cu/L. Iron analyses may require a higher concentration of 700 µg Fe/L and the less sensitive 372.0 resonance nm line, depending on how much is present in the sample.

| Field | Food |
|-------------------|---------------------------------|
| Sample Matrix | Palm Oil |
| Key Element | Pb |
| Reagents Required | 2,6-Dimethylheptan-4-one (DIBK) |

Sample Preparation

Weigh palm oil (1 g) into a 5 mL volumetric flask. Dissolve in DIBK and make up to the mark. Using an infrared lamp to melt the sample facilitates weighing and a warm ultrasonic bath facilitates dissolution. (346)

Standard Preparation

Organometallic standard supplied in a base oil and diluted in DIBK to give a working concentration of 40 µg Pb/L.

Calibration Procedure

Use a pyrolytic platform and calibrate by standard additions technique. A sample volume of 5 µL is recommended. The sample is spiked with 2 and 4 µL of standard. DIBK blank is added to give a constant total volume.

Notes

Total dispensed volume should not exceed 15 µL. If an autosampler is used, the rinse solution can be an aqueous mixture of Triton X-100 (0.01% v/v) and nitric acid (0.1% v/v, 0.02 M). A reduced slit height is recommended.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Pb | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|--------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 80 | 5 | 3.0 | Argon | Dry stage |
| 2 | 150 | 20 | 3.0 | Argon | 15 µL total volume |
| 3 | 180 | 10 | 3.0 | Argon | |
| 4 | 180 | 10 | 3.0 | Argon | |
| 5 | 550 | 10 | 3.0 | Argon | Ash stage |
| 6 | 550 | 30 | 3.0 | Argon | |
| 7 | 550 | 2 | 0 | Argon | Gas stop |
| 8 | 2800 | 1.2 | 0 | Argon | Atomize stage |
| 9 | 2800 | 2 | 0 | Argon | |
| 10 | 2800 | 2 | 3.0 | Argon | Tube clean |
| 11 | 40 | 14 | 3.0 | Argon | Cool down |

Read Command: Steps 8 to 9

Ramp Step: 8. Enter 0 for Maximum Ramp (2000 °C/s)

Mineralogy, Geochemistry and Metallurgy

There is considerable interest in the analysis of trace metals in minerals either from the economic viewpoint of the metal itself, or from the trace metal acting as an indicator to another ore body.

Graphite furnace AA is important when the level of the metal is too low to be measured by conventional flame AA. Typical samples include: metals, minerals, coal, ores and ore concentrates. Many analyses for trace metals in these samples can be accomplished using flame AA; however there are cases where the flame method is not sensitive enough and/or the sample solution contains a high concentration of dissolved salts which tend to clog the burner or nebulizer. The sample can be diluted, but then the analyst re-encounters the flame sensitivity problem. Furnace atomization can be used in many cases to alleviate the necessity of further sample preconcentration.

There have been many reports of the direct analysis of solid samples but this is not often applicable to many samples because of inhomogeneity. Introduction of a small quantity of solid sample into the graphite tube is a difficult procedure. Solid sampling has been successfully applied to the analysis of lead in steels and nickel-based alloys (137), and to a wide variety of metallurgical and biological samples as reviewed in reference 136. Direct analysis of silver in powdered silicate rocks has been reported (138).

For most samples pre-treatment is essential. Even for sensitive graphite furnace techniques, it may be necessary to solvent extract the metal to separate it from the bulk of the sample matrix, and also to provide some degree of concentration. Solvent extraction techniques have been discussed in the Water Analysis section (Chapter Seven).

Geochemical Sample Treatment

Samples must be finely ground and mixed very thoroughly. A large enough sample should be taken to ensure that it is representative of the entire sample. Usually 10 grams is sufficient.

Two general trace metal extraction procedures apply: acid leaching and solvent extraction.

- a** Acid leaching is accomplished by boiling the sample in aqua regia. The sample is generally boiled to near dryness and the salts are dissolved in dilute nitric acid. The sample is filtered through acid-washed filter paper and diluted to an appropriate volume with dilute nitric acid (hydrochloric acid may be substituted if the determination is for precious metals) (139).
- b** Solvent extraction can be used to extract trace metals from geological samples. Extraction procedures are generally specific to only a few elements using any given extraction scheme (140). Further examples of solvent extraction methods are covered in the water analysis section (Chapter Seven).

Specific examples of metal analysis in a variety of geological materials are given in references 141 - 144.

Gold, for example, is often extracted from an acidic solution as the tetrachloroaurate ion/complex complex into methyl isobutylketone to provide a large concentration factor. Amyl acetate has also been used to extract the tetrabromoaurate ion/complex (350), while a rapid method for the extraction of gold and silver into MIBK has been described (351). A comparison between MIBK and diisobutylketone (DIBK) for the extraction of gold from acidic solutions recently favoured MIBK. The presence of co-extracted iron necessitated background correction (352).

Tin has often been a difficult metal to determine by furnace AA, largely because of its stability in solution. Recent work on the determination of tin in rocks has indicated that ascorbic acid modifier and platform should be used (353). It was also suggested that the organic solvent used for tin extractions should not contain chlorine, e.g. MIBK was suitable. Standard reference materials are available for a few geological sample types (145). In cases where reference materials are unavailable the method of standard additions is recommended to compensate for possible chemical interferences.

In metallurgy, the presence of trace levels of several low melting point elements may be harmful to the strength of high temperature alloys. The annealing properties of non-ferrous metals and some metallurgical properties of steels are dependent on the levels of particular trace metals.

The analysis of elements such as arsenic, selenium, lead, bismuth, aluminum and antimony is very important. The vapor generation technique has been applied successfully for some metals in steels (146), but the vapor generation technique exhibits inter-element interferences which may be a problem in the presence of such high concentrations of other metals (147, 148).

Furnace atomization has been used for the determination of arsenic and selenium in high purity copper (148, 149), and for lead, bismuth, selenium, tellurium and thallium in high temperature alloys (150).

The GTA-95 has been used successfully for the determination of several metals in high purity copper using a pyrolytic platform (354). The copper was simply dissolved in nitric acid and arsenic, tin, lead, antimony, bismuth, selenium and tellurium were measured in the solution. Background interferences were minimized by using the platform.

Aluminum (151) and arsenic, antimony and tin (152) have been analyzed in steels following a simple dissolution technique in nitric acid.

Metallurgical Sample Preparation

Samples must be accurately weighed into a PTFE beaker and then dissolved in appropriate acid(s) by gently heating the mixture. Nitric acid (1:1) is generally adequate unless the sample contains a large amount of silica, in which case a nitric-hydrofluoric acid mixture will usually suffice. Reference standards should be treated in the same manner. If reference standards are not available use the method of standard additions.

Plating solutions can be analyzed directly, or diluted with dilute acid or water'. Since the concentration of trace metals in plating solution is generally relatively high, the use of a less sensitive wavelength or a sample dilution (or both) are often necessary.

WARNING



Noxious Fumes

Do not dilute cyanide plating solutions with acid. Highly toxic fumes of hydrogen cyanide would be liberated.

Analytical Examples

The determination of cerium by AA has always been difficult even by flame AA. In furnace AA there is a strong tendency to form the carbide which was overcome by using a tantalum foil lining in a GTA (355). Several international geological reference materials were analyzed to confirm the accuracy of the method described.

Further studies by the same author yielded a procedure for the determination of the rare earths yttrium and scandium in silicate rocks by the GTA in which a tantalum foil lining was also used (356).

Antimony has been measured in geochemical samples by furnace AA using a variety of matrix modifiers (299). Without a modifier antimony was lost at a relatively low temperature of 700 °C in hydrochloric acid solutions. Palladium was found to be a desirable modifier with added benefits from ascorbic acid as well. Severe iron spectral interferences at the 217.6 nm antimony wavelength found with deuterium background correction was expected to be eliminated by the Zeeman technique.

Indeed, the Zeeman technique was shown to overcome spectral interference from nearby matrix lines (cobalt, iron, nickel, chromium) in the measurement of selenium in nickel based alloys (357).

The Zeeman furnace technique with a platform was applied to the determination of arsenic, selenium, chromium, cobalt and nickel in geochemical samples (358). Good agreement was obtained for these elements with a number of geological samples and the Zeeman background correction technique was able to eliminate some spectral interferences which would otherwise appear with the deuterium arc system.

Phosphorus in steel has been determined with a Zeeman furnace technique using lanthanum as modifier (359). A spectral interference which affects the deuterium background correction technique was not present with the Zeeman technique.

Miscellaneous and Industrial

The application of graphite furnace atomization to the analysis of important trace metals in chemicals, organic liquids, paper and pulp products, plastics, acids, etc. is extensive. Sample treatment procedures vary from simple dilution in a suitable solvent, to digestion of solid samples to permit their introduction into the graphite furnace.

Direct analysis of solid samples, although possible, is undesirable for a number of reasons:

- Sample homogeneity is of major concern and therefore it is difficult to obtain a small yet representative sample. It is preferable to digest a much larger sample in appropriate acids and other reagents as required. A small volume is then analyzed by the graphite furnace to provide a more accurate result.
- It would be difficult to weigh a small sample accurately and deposit it into the graphite tube.
- A powdered sample may disperse in the graphite tube, due to the flow of inert gas through the tube, although addition of a liquid reagent would minimize this potential problem.

Digestion procedures for a variety of materials are covered in references (72, 73), Liquid samples of appropriate viscosity may be injected directly into the furnace but some precautions need to be observed, especially with organic solvents. Selection of the correct drying parameters is of particular importance, and depends on the viscosity of the liquid. The pyrolytic coated partitioned tube is especially designed to contain the liquid in the central region of the tube, with little risk of the sample spreading. Further reading on this subject may be found in Chapter Three.

Furnace atomic absorption has been employed in a variety of interesting miscellaneous applications which are covered in references 153 - 158. Other specific methods are summarized in references 118 and 124.

Analytical Examples

The measurement of low levels of silicon is of special importance in the electronics industry. Even very low levels of contaminants can cause a high rejection rate. Parts per billion levels of silicon in deionized process water have been determined by a GTA-95 using the multiple injection facility of the autosampler to provide enhanced sensitivity (360).

It is necessary to monitor and control the levels of various metals in saturated brine used in chlor-alkali plants. A GTA-95 has been used successfully to measure calcium and iron directly in brine (361).

| Field | Industrial, brine electrolysis |
|--------------------|---------------------------------|
| Sample Matrix | Saturated brine, depleted brine |
| Key Element | Fe |
| Also Applicable to | Ca, Ni |
| Reagents Required | Deionized distilled water |

Sample Preparation

Acidify the samples with 0.5% nitric acid (361).

Standard Preparation

Aqueous standards: Standard stock 1000 mg Fe/L in 1 M nitric acid. Prepare 50 µg Fe/L standard.

Calibration Procedure

By concentration technique. Use 2, 5 and 10 µL of standard and blank to maintain a total volume of 10 µL.

Notes

Use a sample volume of 10 µL to avoid excessive drying times. Environmental contamination is a particular problem with calcium. A filtered air room is recommended.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Fe | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|--------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 95 | 5 | 3.0 | Nitrogen | Dry stage |
| 2 | 95 | 12 | 3.0 | Nitrogen | 10 µL total volume |
| 3 | 110 | 50 | 3.0 | Nitrogen | |
| 4 | 125 | 23 | 3.0 | Nitrogen | |
| 5 | 165 | 25 | 3.0 | Nitrogen | |
| 6 | 280 | 20 | 3.0 | Nitrogen | |
| 7 | 490 | 23 | 3.0 | Nitrogen | Melt stage |
| 8 | 700 | 18 | 3.0 | Nitrogen | |
| 9 | 850 | 2 | 3.0 | Nitrogen | |
| 10 | 1080 | 0.5 | 3.0 | Nitrogen | |
| 11 | 1200 | 17 | 3.0 | Nitrogen | Ash stage |
| 12 | 1200 | 10 | 3.0 | Nitrogen | |
| 13 | 1300 | 0.5 | 3.0 | Nitrogen | |
| 14 | 1300 | 15 | 3.0 | Argon | |
| 15 | 1300 | 1 | 0 | Argon | Gas stop |
| 16 | 2300 | 0.7 | 0 | Argon | Atomize stage |
| 17 | 2300 | 1 | 0 | Argon | |
| 18 | 2700 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 16 to 17

Ramp Step: 16. Enter 0 for Maximum Ramp (2000 °C/s)

Other Elements

The procedure for nickel is identical to that for iron. For calcium, use a standard of 20 µg Ca/L and an atomize temperature (steps 16 and 17) of 2600 °C.

| Field | Industrial, semiconductor |
|-------------------|--|
| Sample Matrix | Deionized process water |
| Key Element | Si |
| Reagents Required | Ultra-pure water as a blank and diluent. |

Sample Preparation

As the sample is very pure water, scrupulous care must be taken to ensure no contamination occurs. Use only thoroughly cleaned plastic containers for storage (360).

Standard Preparation

Aqueous standards: Standard stock 1000 mg Si/L and dilute using plastic ware preferably, to give a final working volume of 1 µg Si/L.

Calibration Procedure

By concentration technique. The ultra-pure water is used as a blank.

Notes

Pre-concentration is necessary. The multi-inject facility of the sampler is used to concentrate the solutions in situ. Ten 50 µL aliquots are injected, each aliquot being dried before the next one is dispensed. For all but the last injection, the temperature program is stopped after step 3. After the last injection, the temperature program continues to completion atomizing the pre-concentrated solution.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Si | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|----------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 70 | 3.0 | Argon | 50 µL sample volume. |
| 3 | 120 | 10 | 3.0 | Argon | Multiple injection |
| 4 | 120 | 2 | 0 | Argon | Gas stop |
| 5 | 2700 | 1.3 | 0 | Argon | Atomize stage |
| 6 | 2700 | 2 | 0 | Argon | Atomize stage |
| 7 | 2700 | 5 | 3.0 | Argon | Melt stage |

Read Command: Steps 5 to 6

Ramp Step: 5. Enter 0 for Maximum Ramp (2000 °C/s)

Last Dry Step: 3. Number of injections: 10

Petroleum

Since its introduction the graphite furnace has been widely used in the analysis of petroleum products for trace elements (159-165). Flame atomic absorption is still recommended for the determination of the major metals (Na, Ca, Fe, Zn) and furnace techniques for trace metals (166). For background information on the various applications of atomic spectroscopy to the petroleum industry a review by Buell is suggested (167), while specific methods can be obtained by consulting 'Annual Reports on Analytical Atomic Spectroscopy' which has a dedicated section on petroleum products. (See Appendix 4).

A comprehensive text for the determination of trace metals in petroleum is presented in reference (165) and was prepared from papers presented at the symposium 'Analysis of Petroleum for Trace Metals' held at the 169th National Meeting of the American Chemical Society. Listed in the publication are methods developed by five petroleum companies for 13 elements of environmental interest (As, Be, Cd, Cr, Co, Pb, Mn, Hg, Mo, Ni, V, Se, Sb) using vapor generation, flame and the carbon rod atomizer. The methods are well documented, easy to implement and extensively referenced.

Further information encompassing sampling, standards and methodology are presented in references (168-178).

There are three major areas where furnace techniques can be used in the analysis of petroleum products, namely crude oil, fuel and lubricant, and wear metal analysis. In most cases the sample treatment is similar for all three types of samples.

Crude Oil Processing

The quantity of metals present in crude oil from natural sources can affect the economic processing of the oil, typical elements being sodium, vanadium, iron and nickel. The presence of sodium usually as sodium chloride can occur naturally or it may be picked up as contamination during transportation from the oil well to the refinery. Sodium is analyzed by either flame atomic absorption or emission.

Vanadium present in crude oils and ultimately in fuel oils can combine to form eutectic mixtures which can create severe corrosion of engines or refractory materials in furnaces leading to costly shutdown. Iron and nickel act as catalyst poisons and result in expensive and sudden shutdown of processing plants unless their concentration in the oil is monitored and kept below defined levels.

In most cases the sample is diluted with an appropriate metal-free organic solvent and injected on to the furnace.

Refined Fuels and Lubricants

A wide variety of metals are added to petroleum products to improve the performance of the oil, i.e. zinc compounds are added to oils as antioxidant/antiwear agents; lead is added to gasoline for octane number improvement and knock prevention. The expense of these metal additives and the concentration required for given performance level both require close monitoring of the metal level.

Wear Metal Analysis

The metal analysis of used lubricating oils in engines can provide large economic savings in the prevention of complete mechanical failure. The regular analysis of oils for a range of elements, i.e. Fe, Cu, Ag, Al, Si, Cr, Sn and Pb is carried out and any sudden change in concentration of a particular element can indicate wear before the wearing component fails completely.

It should be pointed out, however, that sudden mechanical failure cannot be predicted, but a sudden increase in the trace metal concentration of the lubricating oil can be an indication of imminent mechanical failure.

The conventional flame technique can provide rapid and simple analysis of most metals in light oils, but viscous oils must be appreciably diluted prior to aspiration into the flame (166). The concentration of the trace metal is consequently low and often close to the detection limit of the flame. The necessity to match the viscosities of sample and standard limits the usefulness of flame atomic absorption for routine wear metal monitoring. This is not a problem with the furnace because sample aspiration is eliminated.

Brodie and Matousek (159) have reported using aqueous standards for standardization. This can be recommended for wear metal analysis because accurate analyses are not a primary requirement. Aqueous standards usually provide an answer within 10–20% of the true value. Organometallic standards should be used if accuracy better than $\pm 20\%$ is a requirement. One problem can exist when applying the furnace to wear metal analyses. Used lubricating oil often contains metal particulates.

It is essential that the sample be free of suspended material before the furnace sample is taken, otherwise the likelihood of an inaccurate answer due to contamination is very great.

Sample Treatment

There are three sample preparation methods presently being employed for the determination of metals in petroleum products.

- 1 Dilution of the oil sample in an organic solvent such as methyl isobutyl ketone (MIBK) or mixed solvent system such as toluene and glacial acetic acid.
- 2 Ashing of the oil sample and dissolution with an appropriate acid.
- 3 Acid digestion.

Each method of sample treatment has advantages and disadvantages and the choice depends on the aims of the analysis, the nature of the sample and elements being analyzed. Ashing and acid digestion are lengthier procedures than simple dilution of the oil, but give total metal contents.

Dilution of the Oil Sample

The dissolution of the oil sample in an organic solvent is fast and simple. Furnace techniques are extremely sensitive and some dilution may be required in order to gain the optimum response. Moreover, the sample, as in the case of used engine oil, may be viscous and require thinning to permit dispensing.

The degree of dilution and choice of solvent will depend on the nature of the sample, the expected level of the element of interest and the background signal appearing during atomization. There is very little restriction on the choice of solvent that can be used to dissolve an oil sample for furnace analysis because of the small volume required for analysis. However, the volatility of the solvent plays an important role in the selection of drying conditions and use of an autosampler.

Where evaporation is a problem, the container should be sealed and sample dispensed manually or an alternative solvent employed. Mixed solvent and emulsion systems allow the use of inorganic salts for the preparation of standards and calibration curves (172, 180). Both emulsion and mixed solvent procedures have been employed for flame atomic absorption, but there is no reason why these sample preparation methods cannot be employed for furnace methods within the restraints of background signal generated after sample treatment. The mixed solvent used to investigate additives (Ca, Mg and Zn) in oil was a toluene-glacial acetic acid mixture (1+4v/v). However, the toluene glacial acetic acid system (100 mL) can only accommodate a maximum of 1 g of a used oil sample which is dissolved in the toluene prior to adding the glacial acetic acid. The solution is stable for analysis for about 2 days. A sample containing 0.5 g oil is completely dissolved and stable for a longer period.

Table 10 lists a number of organic solvents commonly used in oil analyses together with their respective boiling points which can be used as a guide for setting the drying conditions for the furnace. Most solvents can be dried with maximum gas flow at temperatures set below their respective boiling points. For a 20 μ l sample a temperature setting of 80% of the boiling point temperature and a 60 seconds dry has been found to be adequate in most analyses. The dispensing characteristics of the solvent should be investigated prior to analysis in order to determine the maximum injection volume. The dispensed volume will vary depending on the surface tension of the solvent; generally this volume will be between 20 μ L and 40 μ L.

Table 10. Boiling points of organic solvents (178)

| Solvent | Boiling Point °C | Specific Gravity |
|-----------------------------------|---------------------|------------------|
| Kerosene | 175–325 | 0.78 |
| Tetrahydronaphthalene (Tetralin) | 207 | 0.97 |
| Shellsol T | 186–214 | 0.75 |
| 2,6-dimethyl, heptan-4-one (DIBK) | 166 | 0.81 |
| Cyclohexanol | 161 | 0.96 |
| 3-heptanone | 148 | 0.82 |
| m-xylene | 139 | 0.80 |
| Iso-amylalcohol | 132 | 0.81 |
| 4-methyl-pentan-2-one | 118 | 0.79 |
| Toluene | 112 | 0.86 |
| 2-methyl, propan-1-ol | 108 | 0.78 |
| Propan-2-ol (isopropanol) | 83 | 0.78 |
| Carbon tetrachloride* | 77 | 1.59 |
| Tetrahydrofuran* | 65 | 0.88 |
| Chloroform* | 62 | 1.47 |

*Unsuitable for flame atomic absorption

Ashing of Oil Samples

The procedure for ashing oils is based upon the method by Milner Glass, Kirchner and Yurick (179). The sample volume for decomposition will be determined by concentration of the metals of analytical interest in the sample. The analytical procedure for the analysis of iron is described as follows.

The oil sample (2 g) was treated with concentrated sulphuric acid (2 g) and heated on a hot plate until dry in a vycor crucible. The crucible was transferred to a muffle furnace and ashed at 550 °C until all traces of carbon were removed. This was indicated by the absence of a charcoal colour and took about 30 minutes. After cooling the sample was treated with concentrated hydrochloric acid (6 mL) and filtered through a Whatman 541 filter paper. The solution was then made up to 25 ml with distilled water.

Further dilution of the sample stock solution may be required so that the absorption signal lies

with the optimum response range (0.05–8 Abs). The ashing method will give total metal content which represents the sum of particulate and soluble metal. However, volatile metals such as lead and selenium will be lost during the ashing process. There is evidence that cadmium will be retained at 550 °C as a sulphate. As sulphuric acid is used as a digesting agent, matrix matching or a standard addition may be required to overcome interferences.

Acid Digestion

Acid digestions of oil samples permit the retention of low volatile elements that may be lost during ashing or masked by background interference. An acid digestion of organic matrices has been achieved by Schachter and Boyer (81) and could be applied to oil samples. The PTFE high pressure decomposition vessel has also been used to digest mineral oils and this method could possibly be adapted to the analysis of other petroleum products. The following procedure has been used to digest oil samples with success for furnace.

1 g of oil is weighed into a polypropylene container (125 mL) together with 20 mL of 8 N nitric acid. The container is then sealed and heated in a water bath for 30 minutes. After digestion the container is opened carefully in a fume cupboard and the sample filtered through a Whatman 541 filter paper with washings of distilled water into a 100 mL volumetric flask, which is made up to volume with distilled water. Further dilutions are made to ensure the sample response lies within the optimum working range of absorbance.

The polypropylene container should be pressure tested prior to digestion to ensure the vessel is capable of taking the pressure generated during digestion. Analysis of a representative blank in another container is essential. Aqueous nitric acid standards can be used for calibration; the appropriate analytical conditions are listed in Chapter Four.

The Determination of Chromium in used Oil

A petroleum sample can be very diverse. The sample when dissolved in a solvent may have little background interference and successful ashing of the sample may be achieved at low temperatures and minimal ashing time. In such cases a variety of metals may be determined easily. However, the sample may contain low volatile organic constituents and particulate matter that may require a discrete selection of furnace conditions and sample preparation. The choice of specific conditions will depend upon the level of analyte in the sample, the nature of the sample and the element of interest. The determination of chromium in oil after dissolution in diisobutylketone will illustrate some of the procedures involved in establishing suitable analytical parameters for the graphite furnace. The final set of analytical conditions are presented later in this section.

Setting Ash Temperature

An investigation of the maximum ash temperature was carried out for chromium in the used oil sample (1 g of oil in 100 mL DIBK) by arbitrarily choosing a 5 second ramp (Step 4) after the dry (Step 3) before the ash which was held for 30 seconds (Step 5). The ash temperature was increased in increments of 100 °C from 900 °C. The background signal and chromium atomic signals are monitored, using signal graphics for a 30 μ L sample, presented in Figure 28. To investigate a maximum ash setting it is suggested that a starting temperature of about 0.8 of the recommended maximum ash temperature listed in Chapter Four be used. The maximum ashing temperature can vary extensively depending on the form of the element and background matrix, as exemplified in Figure 29. In the case of chromium in oil an ash temperature of 1150 °C was chosen but a value as high as 1250 °C could have been used.

The criteria for setting the ash temperature was to obtain maximum atomic signal and minimum background signal.

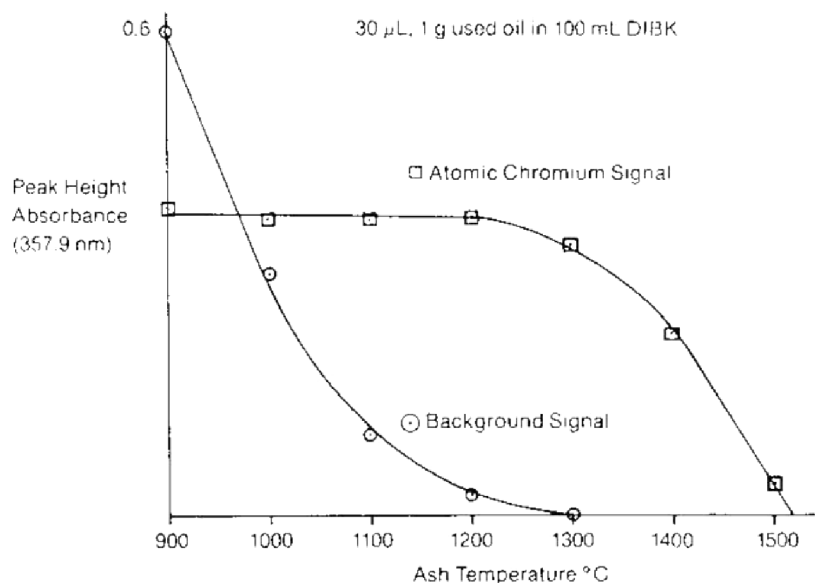


Figure 28. Setting ash temperature

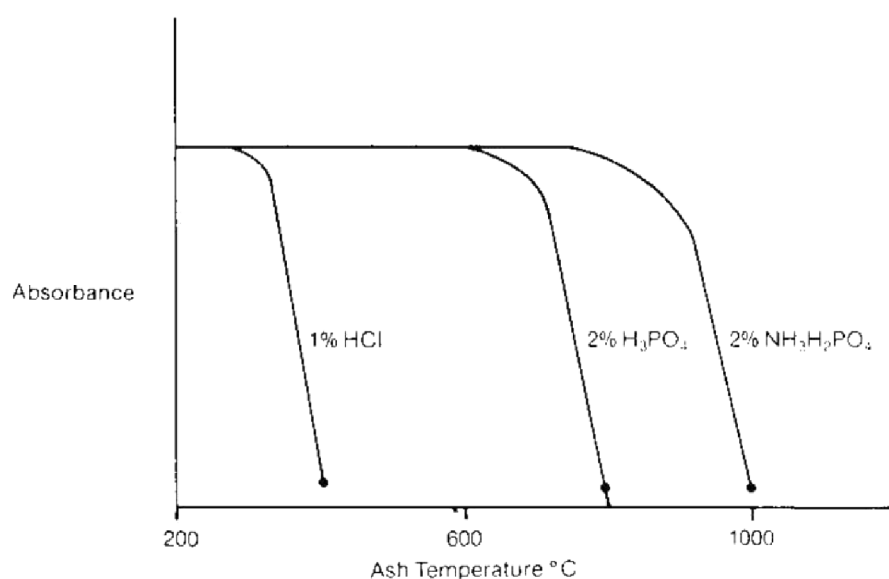


Figure 29. Cadmium in various matrices

Setting of Ash Time

In order to reduce the background signal an adequate ashing time must be set. The ashing time will vary depending on how easily the matrix components can be ashed and removed from the furnace, and the volatility of the analyte element. It may be necessary to ash for a longer period at a lower temperature in order to retain the analyte, providing the ash temperature is sufficient to facilitate adequate ashing of the sample. Figure 30 shows the relationship between the ashing time (Step 5) and the background signal determined at 357.9 nm obtained at 1150 °C and a 30 μL sample of a used oil sample. (1 g used oil in 100 mL DIBK).

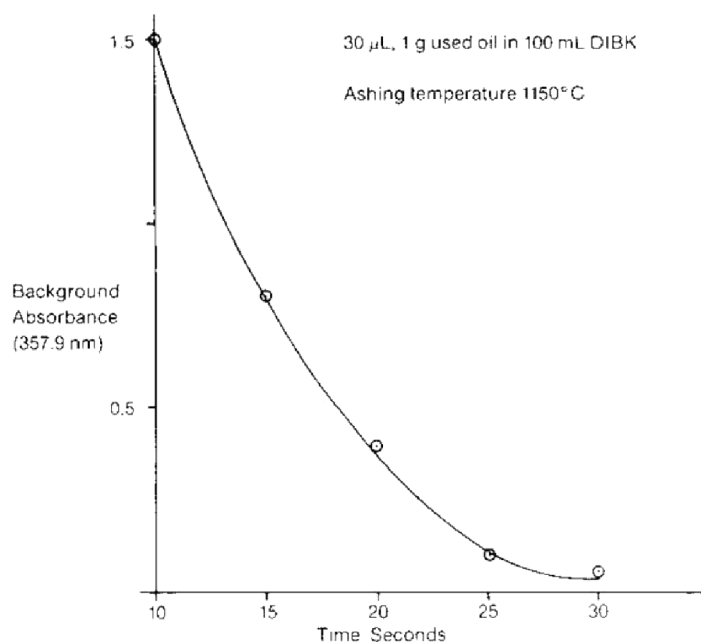


Figure 30. Setting ash time (chromium in used engine oil)

Ramp Rate

In some cases a judicious choice of a slower ramp rate can facilitate separation of background and atomic signals and give better precision. The application of a slower ramp rate will depend on the nature of the sample and the element of interest. For most elements maximum sensitivity is obtained at maximum ramp rate and gas stop during the atomize stage. Figure 31 shows the influence of ramp rate on signal response for chromium in an oil sample expressed as a percentage of the signal at maximum ramp rate.

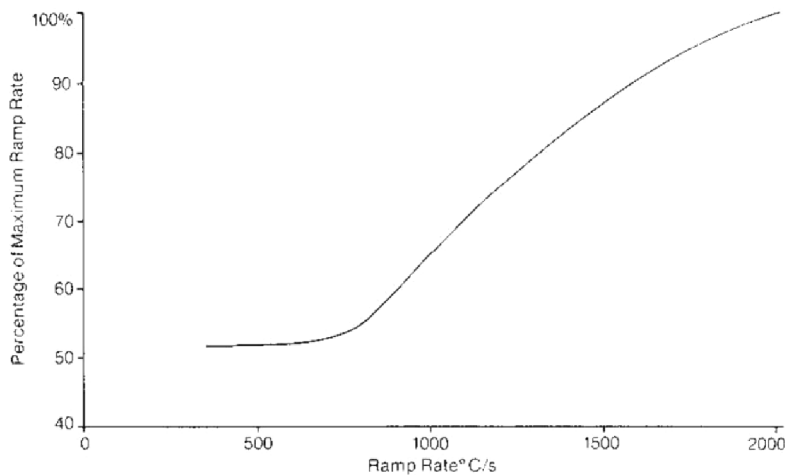


Figure 31. Response for Chromium at various ramp rates (2000 °C = 100%)

An Approach to the Analysis of Petroleum Products

As previously mentioned there are three major sample treatment methods for the determination of elements in petroleum products: dilution of the sample in a solvent, ashing the sample, and acid digestion.

A simple approach to determine which method and form of calibration can be used is achieved by screening the dissolved sample and monitoring the background signal at a number of ashing temperatures.

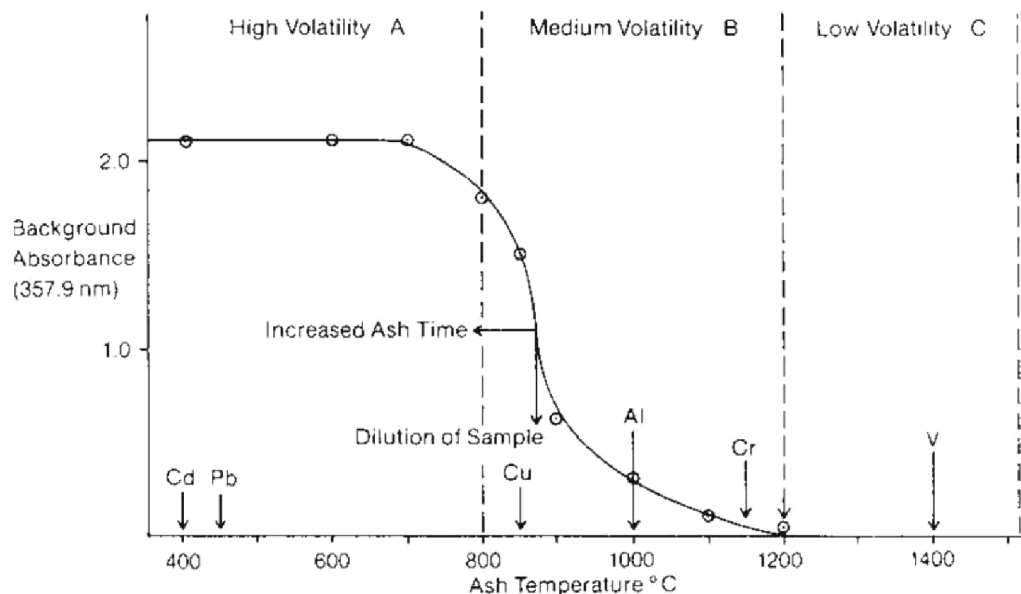


Figure 32. Analysis of used engine oil (1 g oil in 100 mL DIBK)

Each sample will have a characteristic background absorption profile depending on the wavelength at which the background is determined and the nature of the background. In the following example (Figure 32) a great deal of smoke was generated during the ashing stages and the profile found to be independent of wavelength. The elements determined in this study were cadmium, copper, aluminium, chromium and vanadium. Shown in Figure 32, is the background profile for 30 μ L of 1 g of used engine oil dissolved in 100 mL of di-isobutyl ketone (DIBK) and the maximum ashing temperature for each element under investigation for the dissolved oil sample.

Selection of Appropriate Method and Furnace Conditions

In Figure 32 the background profile for the sample varies over an ashing range of 700 $^{\circ}$ C to 1200 $^{\circ}$ C; for a different sample this range could be either higher or lower. Thus the ashing temperature axis can move accordingly, depending upon the sample.

Highly Volatile Elements

In region A highly volatile metals will be atomized together with the background signal as occurred with cadmium in this oil sample. As a result an acid digestion method was employed to determine cadmium. This also permitted the use of aqueous cadmium nitrate standards and the possibility of chemical modification using diammonium hydrogen phosphate to allow a higher ashing temperature. An extraction method could also be applied for these elements as an alternative to acid digestion (160).

Medium Volatility

In region B copper, aluminium and chromium were determined on the diluted sample. Background correction was used and a standard additions method employed to compensate for any matrix or chemical interferences occurring during ashing and atomization. For samples where no chemical interferences are observed and all background effects are compensated using background correction, normal calibration with oil soluble standards could have been employed. An ashing method at 550 °C in a vycor crucible could also have been employed for determination of these elements which would have permitted the use of aqueous standards.

Low Volatility

In region C vanadium was determined in the diluted oil sample and little background signal was present. The use of aqueous standards is possible and normal calibration can be used.

As indicated in Figure 32 increased ashing time in region B will reduce the background signal, moving the profile towards a lower temperature. Further dilution of the sample will reduce the background signal but it will also reduce the analyte concentration. It is always desirable to minimize the amount of the background in the determination of any element.

Analytical Examples

The measurement of several wear metals at low levels in used engine oil has been carried out on a GTA using DIBK as solvent (362). It was preferable to use the pyrolytic platform for lead but the graphite tube was entirely suitable for aluminium, copper, nickel, chromium and vanadium.

A study of the determination of vanadium in heavy industrial fuel oils was carried out on a GTA by Johnson (363). It was found that air ashing facilitated the analysis, but precisions were generally better when air ashing was not included.

An extensive examination of the analysis of aircraft lubricating oils by AA was recently carried out by Saba et al (364). The study included the determination of several metals by flame AA, ICP, DCP and rotating disk AES and concluded that furnace AA was generally superior. Samples were simply diluted 1 in 4 with kerosene and directly injected into the furnace.

Recently the measurement of silicon, tin and titanium in jet engine oils by AA has been detailed by Knowles. Silicon was also measured by flame AA and a comparison made with furnace AA which was clearly superior for low levels of silicon (365). The oil was diluted in MIBK prior to analysis and the graphite furnace was shown to be particularly suitable for the detection of low levels of these elements. Both sensitivity and precision were excellent by furnace AA which permitted the detection of much lower levels than by conventional flame.

A Zeeman furnace AA with platform was used for the measurement of cadmium in crude oil (366). Heavy fuel oils were diluted with carbon tetrachloride and samples were spiked with cadmium for calibration. Oxygen ashing facilitated the removal of ashing products and did not significantly change the lifetime of the graphite tube when a 500 °C ash was employed.

| Field | Petroleum Products |
|--------------------|--------------------------------|
| Sample Matrix | Used Engine Oil |
| Key Element | Cr |
| Also Applicable to | Cu, Ni, Mn, Fe, Al, Ba, Co, Ca |
| Reagents Required | Di-isobutyl ketone (DIBK) |

Sample Preparation

Weigh out 1 g of oil and dissolve in 100 mL of di-isobutyl ketone. Further dilution may be required depending upon sample response.

Standard Preparation

Oil Soluble standards (Chapter Five and Appendix 3).

Calibration Procedure

Standard Additions (Chapter Five).

Notes

A 60% solution of iso-propanol and water was used as a rinse solution. Ensure that the capillary on an autosampler is set well down into the tube. Clearance from the bottom of the tube of 1 mm should be adequate. When using other organic solvents check the boiling point range and set the dry temperature accordingly.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cr | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 80 | 5 | 3.0 | Argon | Dry stage |
| 2 | 150 | 120 | 3.0 | Argon | 30 µL sample |
| 3 | 180 | 20 | 3.0 | Argon | |
| 4 | 1150 | 10 | 3.0 | Argon | Ash stage |
| 5 | 1150 | 35 | 3.0 | Argon | |
| 6 | 1150 | 2 | 0 | Argon | Gas stop |
| 7 | 2500 | 0.9 | 0 | Argon | Atomize stage |
| 8 | 2500 | 2 | 0 | Argon | |
| 9 | 2500 | 2 | 3.0 | Argon | |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

An ash study must be carried out for each element. Initially, set the ash at 75% of the recommended maximum ash temperature listed in Chapter Four. Increase the ash temperature until loss of the analyte is observed then reduce the temperature accordingly. The ash time is also important as a longer ash time allows the ash temperature to be reduced.

| Field | Petroleum Products |
|-------------------|-----------------------------|
| Sample Matrix | Used Engine Oil |
| Key Element | Si |
| Reagents Required | 4-Methylpentan-2-one (MIBK) |

Sample Preparation

Place 1 mL (1.3 g) of sample in a 5 mL volumetric flask. Dissolve in MIBK and make up to the mark. The use of a vortex mixer or ultrasonic bath is recommended (365).

Standard Preparation

Dilute multi-element organometallic standards supplied in an appropriate base oil with MIBK as required.

Calibration Procedure

By standard additions technique. A sample volume of 5 μ L is recommended. The sample is spiked with 5 μ L and 10 μ L of standard using the autosampler. MIBK blank is added to give a constant total volume.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Si | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 40 | 1 | 3.0 | Argon | Dry stage |
| 2 | 80 | 10 | 3.0 | Argon | |
| 3 | 150 | 10 | 3.0 | Argon | |
| 4 | 150 | 60 | 3.0 | Argon | |
| 5 | 1000 | 10 | 3.0 | Argon | Ash stage |
| 6 | 1000 | 10 | 3.0 | Argon | |
| 7 | 1000 | 2 | 0 | Argon | Gas stop |
| 8 | 2700 | 0.9 | 0 | Argon | Atomize stage |
| 9 | 2700 | 2 | 0 | Argon | |
| 10 | 2700 | 3 | 3.0 | Argon | Tube clean |

Read Command: Steps 8 to 9

Ramp Step: 8. Enter 0 for Maximum Ramp (2000 °C/s)

| Field | Petroleum Products |
|-------------------|-----------------------------|
| Sample Matrix | Jet Engine Oil |
| Key Element | Sn |
| Reagents Required | 4-Methylpentan-2-one (MIBK) |

Sample Preparation

Place 1 mL (1.3 g) of sample in a 5 mL volumetric flask. Dissolve in MIBK and make up to the mark. The use of a vortex mixer or ultrasonic bath is recommended (365).

Standard Preparation

Dilute multi-element organometallic standards supplied in an appropriate base oil with MIBK as required.

Calibration Procedure

By standard additions technique. A sample volume of 4 µL is recommended. The sample is spiked with 2 and 4 µL of standard using the autosampler. MIBK blank is added to give a constant total volume.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Sn | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 40 | 1 | 3.0 | Argon | Dry stage |
| 2 | 120 | 10 | 3.0 | Argon | |
| 3 | 800 | 30 | 3.0 | Argon | Ash stage |
| 4 | 800 | 15 | 3.0 | Argon | |
| 5 | 800 | 2 | 0 | Argon | Gas stop |
| 6 | 2600 | 0.9 | 0 | Argon | Atomize stage |
| 7 | 2600 | 2 | 0 | Argon | |
| 8 | 2600 | 3 | 3.0 | Argon | Tube clean |

Read Command: Steps 6 to 7

Ramp Step: 6. Enter 0 for Maximum Ramp (2000 °C/s)

| Field | Petroleum Products |
|-------------------|-----------------------------|
| Sample Matrix | Jet Engine Oil |
| Key Element | Ti |
| Reagents Required | 4-Methylpentan-2-one (MIBK) |

Sample Preparation

Place 1 mL (1.3 g) of sample in a 5 mL volumetric flask. Dissolve in MIBK and make up to the mark. The use of a vortex mixer or ultrasonic bath is recommended (365).

Standard Preparation

Dilute multi-element organometallic standards supplied in an appropriate base oil with MIBK as required.

Calibration Procedure

By standard additions technique. A sample volume of 4 μ L is recommended. The sample is spiked with 2 and 4 μ L of standard using the autosampler. MIBK blank is added to give a constant total volume.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Ti | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 40 | 2 | 3.0 | Argon | Dry stage |
| 2 | 80 | 30 | 3.0 | Argon | |
| 3 | 80 | 10 | 3.0 | Argon | |
| 4 | 150 | 10 | 3.0 | Argon | Ash stage |
| 5 | 1400 | 15 | 3.0 | Argon | |
| 6 | 1400 | 15 | 3.0 | Argon | |
| 7 | 1400 | 2 | 0 | Argon | Gas stop |
| 8 | 2900 | 0.8 | 0 | Argon | Atomize stage |
| 9 | 2900 | 2 | 0 | Argon | |
| 10 | 2900 | 3 | 3.0 | Argon | Tube clean |

Read Command: Steps 8 to 9

Ramp Step: 8. Enter 0 for Maximum Ramp (2000 °C/s)

| Field | Petroleum Products |
|-------------------|---------------------------|
| Sample Matrix | Industrial Fuel Oil |
| Key Element | V |
| Reagents Required | Di-isobutyl ketone (DIBK) |

Sample Preparation

Weigh out 1 g of oil and dissolve in 100 mL of di-isobutyl ketone. Further dilution may be required depending upon sample response.

Standard Preparation

Use oil soluble standards. Aqueous standards may be used in the absence of oil soluble standards.

Calibration Procedure

Normal standard calibration with three standards over the optimum absorbance range.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element V | | | Furnace Operating Conditions | | |
|---------------|------------|------------|------------------------------|----------|--|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 80 | 10 | 3.0 | Argon | Dry stage, set for even drying. 30 µL sample |
| 2 | 150 | 120 | 3.0 | Argon | |
| 3 | 180 | 20 | 3.0 | Argon | |
| 4 | 1400 | 10 | 3.0 | Argon | Ash stage |
| 5 | 1400 | 40 | 3.0 | Argon | Analyte should be checked for loss |
| 6 | 1400 | 2 | 0 | Argon | |
| 7 | 2800 | 0.7 | 0 | Argon | Atomize stage |
| 8 | 2800 | 2 | 0 | Argon | |
| 9 | 2800 | 2 | 3.0 | Argon | |
| 10 | 40 | 8 | 3.0 | Argon | Cooling step |
| 11 | 2800 | 1.4 | 3.0 | Argon | Tube clean |
| 12 | 2800 | 2 | 3.0 | Argon | |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Water Analysis

Introduction

Most atomic absorption analyses are carried out on aqueous samples. Although emphasis in this section is specifically concerned with environmental samples, many of the techniques mentioned are commonly used in the analysis of a variety of sample types.

Environmental scientists are demanding more of the analytical chemist in their quest to understand the complex relationships existing between trace metals and living organisms. Current water studies are being directed towards the determination and distribution of the various physico-chemical forms of trace metals in natural and waste waters. A trace metal's chemical form and properties will be determined by its interaction with the parent matrix. Environmental water samples are extremely variable in their composition, and information about their origin (whether sea, lake, river or sewage) is essential in determining the approach and techniques used in an analysis. Invariably the analysis will involve the determination of either total metal or trace constituent. The total metal constituent is an absolute value which may not often reflect the biological or environmental activity of a particular constituent. However, if the total constituent is considered in conjunction with other constituents, its role in a particular water sample may become apparent. It is therefore essential that the total trace metal be determined accurately and precisely.

The total metal concentration in water is being used to assess water quality and elucidate transport mechanisms of trace metals. A number of computer programs have now been written to calculate the various amounts of species present at equilibrium in a multicomponent system. The most notable of these HALTAFALL(181), WATEQ(182) and REDEQL(183,184) (MINEQL)(185) all have facilities for handling acid-base, redox and phase equilibrium, and calculate species from gross concentrations of the components and equilibrium formation data. The validity of water models using computer programs is being tested by laboratory speciation studies requiring sensitive analytical techniques (186). With most water samples furnace atomic absorption permits direct analysis of water with no sample preparation. The use of chemical modifiers automatically added by the sample dispenser offers significant advantages for many elements (see Chapters One and Eight).

Water analysis is a very diverse field. Clear aims and goals should be set and the appropriate method chosen or developed to gain the information required. There are two main areas currently being pursued in water analysis, namely speciation studies and water quality monitoring. For further background on the importance of water and water analysis in these areas, specific texts and journals should be consulted (Texts 187-194, References 194-224),

Speciation Studies

In natural and effluent water samples, the task of speciation is now being tackled (192, 193, 242, 243). The ultimate aim is to find the total chemical and biochemical makeup of an entire lake, stream, estuary or sea system. Metals in natural waters can exist in the following forms:

Table 11. Metal species in natural waters

| | Species Size (diameter nm) |
|---|---------------------------------------|
| Free hydrated ions | |
| Inorganic complexes and ion pairs | |
| Organic complexes and chelates | up to 1 |
| Metal species bound to high molecular weight organic material | |
| Metal species in the form of highly dispersed colloids | up to 10 |
| Ions or compounds adsorbed onto colloids | |
| Precipitates, large organic particles | up to 100 |

All these species are in a dynamic state and are affected by the composition of the background matrix. Factors influencing the distribution of the species include pH and pE, dissolved gases (O₂, CO₂), temperature, sunlight, biota, sedimentary material and ionic strength (salinity) (187, 190, 192-194).

A number of separation techniques, in conjunction with atomic absorption, are being used to determine the physico-chemical forms and these can be divided into two major groups which are often used concurrently.

These are:

- Separation of species by size using physical properties of the species;
- Separation of species using specific chemical properties of the species.

Size Separation of Species

A number of techniques allow separation of species over the full range listed in Table 11. However, contamination and the nature of the sample can change with storage time and during the separation process which can be lengthy. Separation techniques being used to determine these various forms of the metal include ultrafiltration, gel filtration, chromatography and dialysis.

An idealized chemical species separation scheme is presented by Burrell (191). Hart and Davies (205, 206) have also separated species using physical techniques and warn against contamination and negatively charged dialysis membranes that may retard the passage of negative species. A typical analysis scheme on a size basis is presented in Figure 33.

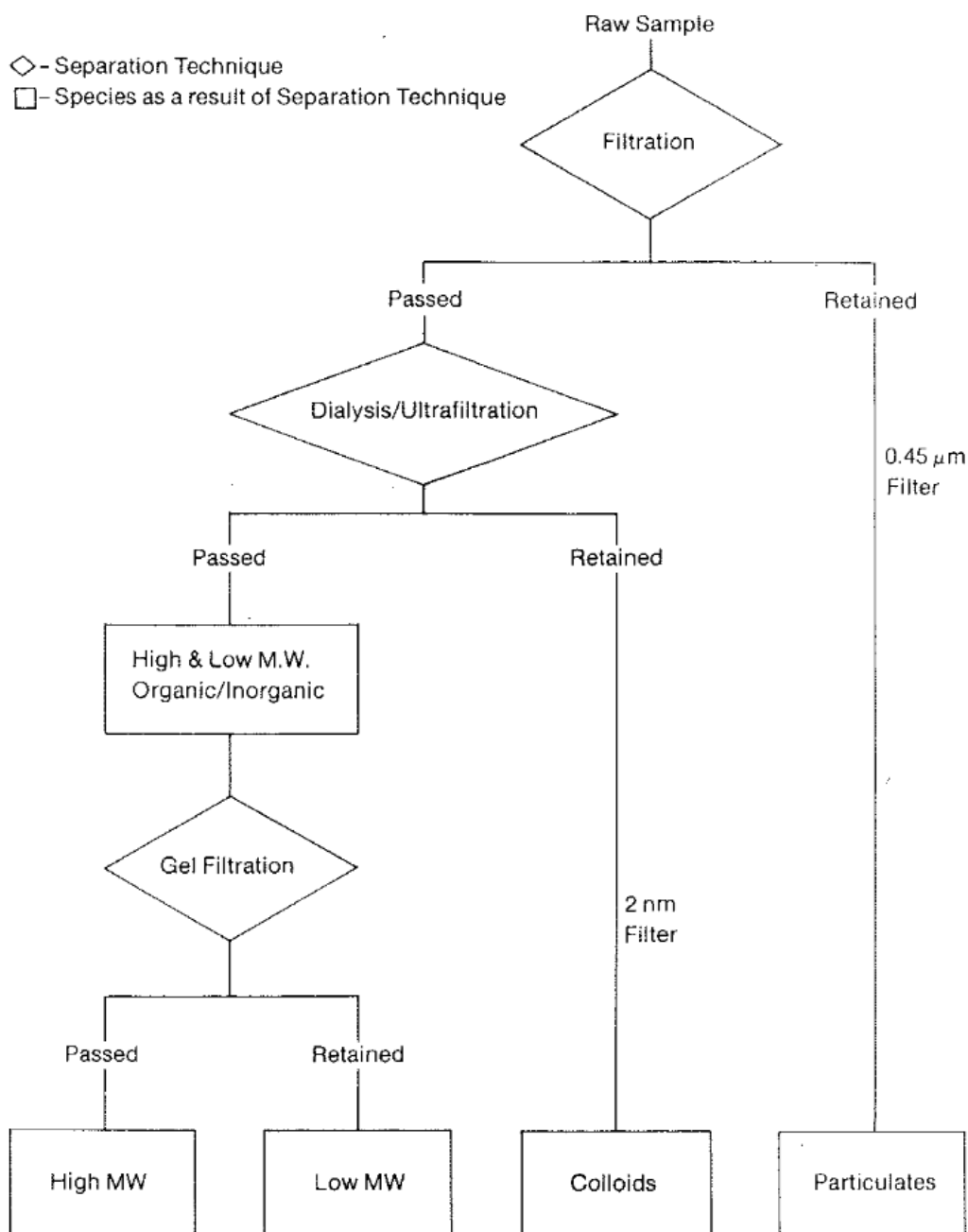


Figure 33. Typical metal speciation scheme

Water Quality Monitoring and Sources of Analytical Methods

Atomic absorption is mainly used to monitor trace metal levels in water. The classes of water which can be directly analyzed on the furnace include: drinking, river and lake waters, effluents and sea water. The major elements (Ca, Mg, Na, Fe, Zn) are generally analyzed by flame atomic absorption while many other trace elements can be determined directly by the furnace with very little sample preparation. Table 12 summarizes the range of some trace elements in U.S. rivers and natural waters (207). Analyses since that time have indicated much lower levels for some elements.

Table 12. Summary of trace elements in waters of the United States

| Element | Frequency of Detection % | Observed Values ($\mu\text{g/L}$) | | |
|---------|--------------------------|-------------------------------------|-------|---------|
| | | Minimum | Mean | Maximum |
| Ag | 6.6 | 0.1 | 2.6 | 38.0 |
| Al | 31.2 | 1.0 | 74.0 | 2760.0 |
| As | 5.5 | 5.0 | 64.0 | 336.0 |
| B | 98.0 | 1.0 | 101.0 | 5000.0 |
| Ba | 99.4 | 2.0 | 43.0 | 340.0 |
| Be | 5.4 | 0.01 | 0.19 | 1.22 |
| Cd | 2.5 | 1.0 | 9.5 | 120.0 |
| Co | 2.8 | 1.0 | 17.0 | 48.0 |
| Cr | 24.5 | 1.0 | 9.7 | 112.0 |
| Cu | 74.4 | 1.0 | 15.0 | 280.0 |
| Fe | 75.6 | 1.0 | 52.0 | 4600.0 |
| Mn | 51.4 | 0.3 | 58.0 | 3230.0 |
| Mo | 32.7 | 2.0 | 68.0 | 1500.0 |
| Ni | 16.2 | 1.0 | 19.0 | 130.0 |
| P | 47.4 | 2.0 | 120.0 | 5040.0 |
| Pb | 19.3 | 2.0 | 23.0 | 140.0 |
| Sr | 99.5 | 3.0 | 217.0 | 5000.0 |
| V | 3.4 | 2.0 | 40.0 | 300.0 |
| Zn | 76.5 | 2.0 | 64.0 | 1183.0 |

There are a number of organizations that have detailed analytical methods available for the analysis of trace metals in a variety of waters and wastes using atomic absorption (208-217) most of which are obtainable from the U.S. Government Printing Office. These methods have arisen as a result of Government legislation concerning the environment (218-220) and form the basis for determining water quality. Modifications to these methods are always being implemented and it is therefore essential that a periodic review of the methods and constant contact with the relevant government department be maintained.

"Annual Reports on Analytical Atomic Spectroscopy" contains a complete section on Waters, Sewage and Effluents and the ASTM has a working document D3919 which specifically covers standard practices for measuring trace elements in water by graphite furnace atomic absorption spectrophotometry (221).

Interlaboratory Water Quality Testing has indicated that there can be considerable inaccuracies obtained when a specific method is employed. Therefore, the United States Environmental Protection Agency (U.S.E.PA) has published the " Handbook for Analytical Quality Control in Water and Wastewater Laboratories" which endeavours to maintain the validity of water data and should be consulted together with the specific methods used {222}. Problems associated with trace analysis (223, 224) have been discussed in Chapter Five.

Definition and Treatment for the Four Types of Metals

The U.S.E.P.A. determine very low levels of trace metals in water samples by direct injection onto the furnace. The samples are treated to give four physico-chemical forms of the metal (209).

- Dissolved Metals: Those constituents (metals) which pass through a 0.45 μm membrane filter.
- Suspended Metals: Those constituents (metals) which will be retained by a 0.45 μm membrane filter.
- Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion, or the sum of the concentrations of metals in both the dissolved and suspended fractions.
- Total Recoverable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid.

Each physico-chemical form has its own specific methodology encompassing sampling and storage procedures.

Sampling

The volume of sample required for each physico-chemical form and the final volume of the treated sample presented for determination will depend upon:

- The approximate level of the metal present in the sample.
- The sample preparation used to analyze the sample.
- The number of metals to be determined in the sample.
- Whether flame, furnace atomization or hydride generation will be used.

Table 13. Summary of trace elements in waters of the United States

| ALL METALS EXCEPT Hg | Recommended Volume, Container | Preserving Agent | Storage Time |
|-------------------------|----------------------------------|--|---|
| Dissolved | 200 P,G | Filter on site HNO ₃ to pH 2 | 6 Months |
| Suspended | 200 P,G | Filter on site | 6 Months |
| Total | 100 P,G | HNO ₃ to pH 2 | 6 Months |
| MERCURY | | | |
| Dissolved | 100 P,G | Filter on site HNO ₃ to pH 2 | 38 days (glass) 13 days (hard plastic) |
| Total | 100 P,G | HNO ₃ to pH 2 | 38 days (glass) 13 days (hard plastic) |

G = Glass, hard or soft (Borosilicate glass preferred).

P = Plastic, hard or soft (Polyethylene with a polypropylene cap (no liner) preferred).

pH 2 is achieved by addition of 5 mL redistilled concentrated HNO₃ per litre of sample.

Reagents

Many of the procedures require quartz distilled deionized water and quartz distilled acid. The preparation of these reagents is described by E. Kuehner et al (63). It must be emphasized that only the purest reagents can be used for trace metal analysis. Blank reagents must be analyzed together with the samples to confirm the blank level of trace metals in the reagents.

Preconcentration Techniques

Solvent extraction and ion exchange are the most popular preconcentration techniques presently used in atomic absorption analysis (252). Both techniques rely on the formation of a specific and selective form of the metal which allows separation of the element from the original sample matrix and concentration into a simpler matrix. Both techniques are simple in application and relatively inexpensive. In furnace atomic absorption, ion exchange and solvent extraction are used to analyze metals in samples, especially when the metal level is very low and significant interferences are evident, such as with sea water. Extreme care must be taken when using the techniques in furnace analysis, as contamination from the reagents and laboratory glassware can be high enough to invalidate the method. However, both methods have been used successfully to determine many elements below 1 ng/mL.

A number of special texts have been published on each technique and should be consulted for further background information (225-228).

Total Metal Determinations using Solvent Extraction and Ion Exchange

In a total metal determination it is necessary to ensure all the metal in the sample is oxidized to the required oxidation state which permits complete solvent extraction or ion exchange. Sample treatment by the addition of oxidizing agents such as persulphate or ceric sulphate may be required (229, 231). However the addition of these reagents may cause contamination. Ozone and ultraviolet light have been used to facilitate oxidation of the sample without contamination (232, 233).

Recovery Studies

The effectiveness of any preconcentration technique relies on the accuracy of the result. Recovery studies using a particular preconcentration method should be carried out on samples of known concentration. The validity of the method can be assessed by determination of known reference standards (234-236).

Solvent Extraction

Ionic compounds show appreciable solubility in water and in general are not soluble in organic solvents, while covalent compounds show preferential solubility in organic solvents. Solvent extraction from aqueous solutions into immiscible organic solvents occurs when an uncharged species is formed. So, in order to extract a particular compound, anion, cation or complex, it is essential for it to be either present as or be able to form a neutral molecule in water. This neutral molecule is normally a metal chelate or ion pair (278).

Speciation Studies using Solvent Extraction

With a complete understanding of the principles of solvent extraction, it is possible to carry out speciation studies on aqueous samples. The relative oxidation states of redox pairs can be determined in the sample by selectively extracting one oxidation state by a judicious choice of the chelating agent.

For example:

As(III), Cr(VI), and Sn(II) are quantitatively extracted by dibenzylthiocarbamic acid into chloroform while As(V), Cr(III) and Sn(IV) are not extracted (225).

The total metal can be determined by ensuring all the metal is either oxidized or reduced to the one extractable form or if present in sufficient quantity determined directly without sample treatment.

Ion Exchange

Ion exchange separates charged species from the bulk matrix on the basis that the ion or charged molecule has a greater affinity for the ion exchanger than the parent matrix.

For atomic absorption the ion exchanger preconcentrates elements and removes matrix interferences. Most ion exchangers consist of a support containing a molecule which shows strong chemical affinity for charged species. The supports vary widely and include cellulose, paper (237), resins (239-241), polystyrene foams, zeolite, graphite (238), glass and aluminosilicates, while the molecule varies depending on the charge of the ion or molecule required. For separation or preconcentration of positive species a cation ion exchanger is required and for negatively charged species an anion exchanger is used. Ion exchange resins allow field sampling and eliminate the collection and storage of large sample volumes.

Relatively large quantities of reagents are often used in ion exchange and these must be extremely clean. The ion exchanger will concentrate the analyte present in the reagents as well as the sample, leading to a positive error.

Speciation Studies using ion Exchange

Ion exchange can be employed to investigate various charged forms of the metal in a sample and their distribution. By running the sample through both an anion and cation exchange resin, it is possible to determine the overall charge distribution of various metal species. The difference between the species exchanged on the strong acid and strong base and their respective weaker analogs can give information on the distribution and stability of the metal species at a particular pH. A speciation scheme using Chelex 100 which could be adapted for atomic absorption has been proposed by Florence and Batley (242).

Special Ion Exchange Resins

A number of special resins with specific ion exchange groups are commercially available (239-241). The most important commercial ion exchanger for the preconcentration of metals is the chelating resin with imidio diacetic groups (242, 243).

This resin has high selectivity for the transition metals and relatively low selectivity for the alkali and alkali earth metals, allowing preconcentration of trace metals in samples such as sea water, with high concentrations of calcium and magnesium that can saturate the sites on a strong acid ion exchanger (244). However, some decrease in efficiency has been observed in the presence of alkali and alkali earth metals with Chelex 100 for the preconcentration of transition elements (248, 249). Exchangers using a chelation principle are pH dependent and must be operated over a regulated pH range as the pH can often change the characteristics of the exchanger, giving it completely different properties to those required for preconcentration (245).

A number of ion exchange resins with specific chelating groups have been prepared for the separation and preconcentration of metals (246-251). The most promising laboratory made resins are a poly(dithiocarbamate) resin capable of quantitatively complexing As, Ag, Cd, Cu, Hg, Ni, Pb, Sb, Zn, Al, Au, Bi, In, Ir, Pd, Re, Rh, Se, Sn, Te and Tl, and poly(acrylaminoxine) resin which has quantitatively sequestered Fe, Mn, Cu, Co, Hg, Ni, Pb, In, Cd and Ag (246-249). Both the poly(dithiocarbamate) and poly(acrylaminoxine) resins have shown very little affinity for alkali and alkaline earth metals and have been employed to preconcentrate metals from urine, natural waters, sea waters and milk.

Coprecipitation

Ion exchange and solvent extraction techniques are the most predominantly used methods of preconcentration of metal for analysis by atomic absorption (213). A method of preconcentration which is easy in application although not so widespread, is coprecipitation. Coprecipitation essentially concentrates metals by precipitation with an insoluble compound such as aluminium hydroxide. The precipitate can be collected either by filtration or floatation and then redissolved for analysis. Co-precipitation has been used successfully to preconcentrate a variety of trace metals (Cr, Mn, Co, Ni, Cu, Cd, Pb, Zn, Fe) from natural and sea waters (253, 254). A comprehensive list of metals that can be co-precipitated is given by Luke (255).

Miscellaneous Applications

Electrodeposition

Electrodeposition techniques have been applied to the preconcentration of elements (Ag, Hg, Bi, Cd, Cu, In, Pb, Sb, Se and Tl) from high salt matrices (256, 257). The technique has also been used to differentiate between toxic Cr(VI) and less toxic Cr(III) in natural waters (258).

Essentially the metals are either plated out on to the graphite tube which is then mounted into the furnace and atomized, or concentrated on a graphite electrode which is homogenized and small portions atomized. The homogenized approach allows the determination of a number of elements and has the advantage that the homogenized graphite can be stored for any length of time (257).

AA as a Chromatographic Detector

Knowledge of the specific chemical form of an element is becoming increasingly important in a number of fields such as toxicology, biochemistry and the environment. Often the activity of a particular metal is not determined by its total concentration but is dependent upon a form and other species present in the sample. For example Cr(VI) is more toxic than Cr(III) and therefore it is necessary to distinguish between these species. A total determination of Cr will not discriminate between Cr(VI) and Cr(III) and, as a result, the toxic potential of the sample cannot be accurately assessed.

Atomic absorption alone does not allow any differentiation between the various specialized forms of a metal, but coupled to an appropriate separation technique, various species of the metal can be determined (259-264). Both gas and liquid chromatographs have been interfaced to flame and furnace atomic absorption for speciation studies. See Table 14 (155).

Table 14. Atomic absorption speciation studies

| Element | Species | Separation Technique |
|---------|--|----------------------|
| As | Me ₃ As, (C ₆ H ₅) ₃ As | HPLC/GLC |
| Cd | Alkyls in gasoline | GLC |
| Cr | Cr ⁶⁺ and Cr ³⁺ | IE/HPLC |
| Cu | EDTA, NTA, CDTA, EGTA Glycine, Trien | HPLC |
| Hg | Methyl/Ethyl/Phenyl | HPLC/GLC |
| Mn | Mn ⁷⁺ and Mn ²⁺ | IE/HPLC |
| Pb | Alkyl/Phenyl in gasoline | GLC |
| Se | Alkyl/Phenyl | GLC |
| Sn | Alkyl/Phenyl | HPLC |
| Te | — | TLC |
| Zn | Alkyl/Aryl glycine, EDTA, Trien | HPLC |

HPLC – High Pressure Liquid Chromatography

IE – Ion Exchange Chromatography

GLC – Gas Liquid Chromatography

TLC – Thin Layer Chromatography

Sea Water Analysis

The oceans are being used for the deposition of environmental wastes and therefore a great deal of attention has been given to the analysis of trace elements in sea water. Sea water is a challenging matrix for the analytical chemist due to the very low concentrations (188, 265) of many important trace metals (Table 15).

Table 15. Minor components of sea water

| Element | $\mu\text{g/L}$ | Element | $\mu\text{g/L}$ |
|---------|-----------------|---------|-----------------|
| Ag | 0.3 | Mn | 0.7 (b) |
| Al | 0–1900 | Mo | 9–11 |
| Au | 0.004–0.5 | Ni | 0.1–2.6 |
| Ba | 6–90 | Pb | 4 |
| Bi | 0.2 | Rb | 100–200 |
| Cd | 0.03–0.06 | Sb | 0.2 |
| Ce | 0.4 | Sc | 0.04 |
| Co | 0.05–0.7 | Se | 4–6 |
| Cr | 0.04–2.5 | Si | 10–1000 (c) |
| Cs | 2 | Sn | 3 |
| Cu | 1–25 | Th | 0.001–0.1 |
| F | 1400 | Ti | 1–9 |
| Fe | 0–60 (a) | U | 0.3–2.5 |
| Ga | 0.5 | V | 0.2–4.6 |
| Hg | 0.03 | W | 0.1 |
| I | 50 | Y | 0.3 |
| La | 0.3 | Zn | 7–21 |
| Li | 100 | | |

- (a) Iron is largely hydrolysed and is retained on a 0.45 μm filter. Some iron is soluble in dilute acid solution and most is soluble on boiling in strong acid solution.
- (b) Most of the manganese present in sea water is in particulate form, such as from the oxide fallout from volcanic dusts.
- (c) In surface layers, silicon is consumed by diatoms and very little is present in the free form.

Furthermore, the high salt content, mainly sodium chloride, can cause substantial background and chemical interferences in furnace atomic absorption. Two approaches in the elimination and reduction of interferences due to the high content of alkali chlorides have been prevalent in recent studies using the graphite furnace. These are:

- Separation and preconcentration of trace metals from the sea water matrix (266-269).
- Modification of the sea water matrix to eliminate the effect of chloride by converting the metal chloride to another form, thus altering the atomization properties of the analyte and interfering halide salts (51, 270-273).

Separation and Pre concentration

Sturgeon and his co-authors have determined 9 trace elements (Fe, Mn, Cd, Zn, Cu, Ni, Pb, Cr, Co) in sea water by graphite furnace techniques using a mixed chelate solvent extraction and ion exchange as preconcentration methods (266).

The methodology used by Sturgeon et al is comprehensive and addresses many of the typical problems encountered in the analysis of sea water at the ng/L level. Bruland and his co-workers (267) have endeavoured to implement sample collection procedures for the analysis of zinc, nickel, copper and cadmium in sea water in an effort to gain meaningful data. In this study a solvent extraction using dithiocarbamate was compared to results obtained using the ion exchange resin Chelex 100. The chelex values for copper and nickel were found to be substantially lower than for the solvent extraction which confirms previous work (243). The methods used by Bruland and his co-workers can be used for other trace metals which can be preconcentrated by dithiocarbamate or Chelex 100.

Chemical Modification of Sea Water

A number of investigations have been carried out on modifying sea water matrix to change the volatilization characteristics of both the analyte and interfering sodium chloride. Many studies have dealt with the elimination of the non-specific component using ammonium nitrate which permits ashing of ammonium chloride and sodium nitrate at a much lower temperature than sodium chloride. Nitric acid has also been used to facilitate the removal of the sea water matrix, again by forming sodium nitrate.

Ammonium dihydrogen phosphate has been used to provide analyte stability for Cd, and combined with nitric acid is particularly useful in the sea water matrix (293, 376).

More recently organic chemical modifiers such as ammonium oxalate, have been used on sodium chloride matrices to reduce interferences (273, 51). Studies with organic modifiers have shown that isolation of the element in one specific form or complex as well as reduction of the background interferences can be achieved to ensure more accurate and precise determinations.

With the Zeeman graphite tube atomizer it is possible to observe the corrected atomic signal and the Zeeman background signal simultaneously with signal graphics. This information is extremely valuable in furnace program development and in the appropriate selection of modifier conditions (such as volume and concentration).

From information obtained with such a study it is possible to determine the maximum ash temperature and preferred atomization temperature, and to select the optimum conditions for the analysis.

A good example is in the analysis of sea water for cadmium using ammonium dihydrogen phosphate and nitric acid as a chemical modifier.

The cadmium determination in sea water was carried out using the pyrolytic platform in a plateau tube. The platform is particularly useful for the determination of this volatile analyte. High levels of non-specific absorption can be expected as high ashing temperatures cannot be employed without analyte loss. When the platform technique is combined with appropriate matrix modification the background levels are substantially decreased and trace levels of cadmium in sea water can be determined.

A 2% ammonium dihydrogen phosphate reagent was extracted to remove cadmium and then combined with high purity nitric acid in the volume ratio 70:30. Figure 34 shows that there was very little cadmium remaining in the chemical modifier.

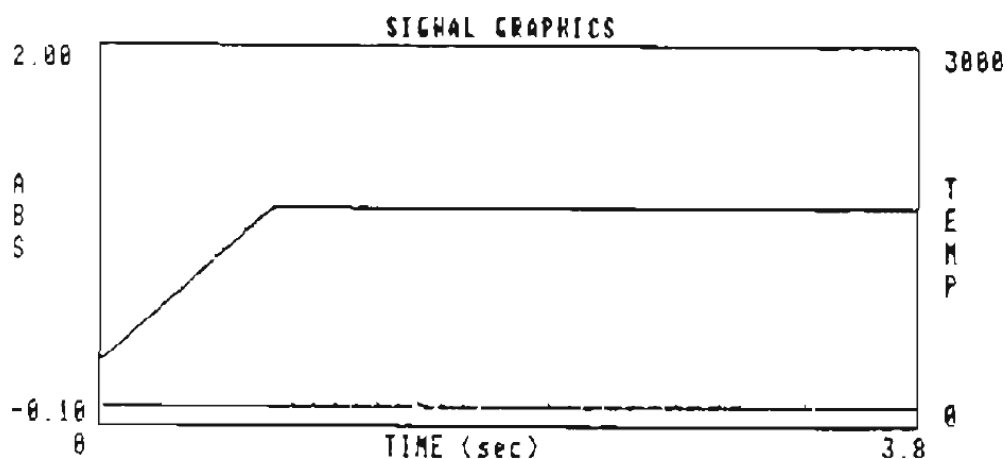


Figure 34. Blank signal from chemical modifier

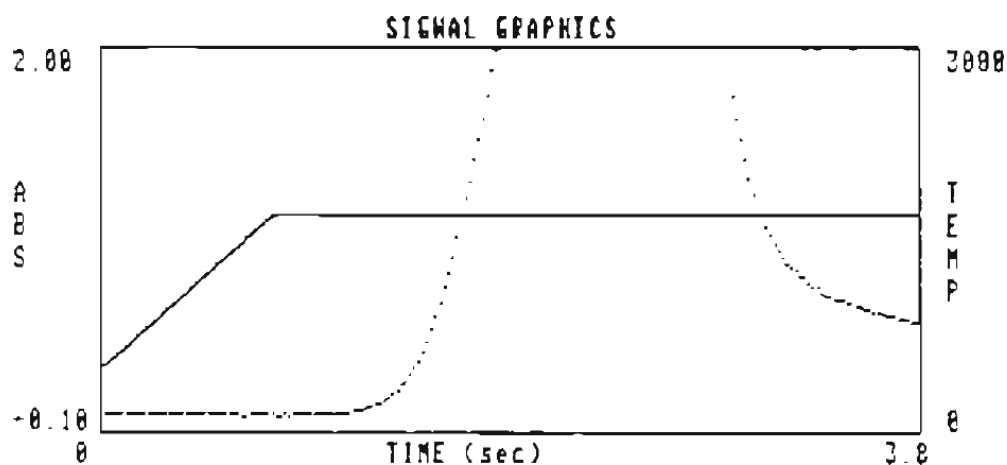


Figure 35. Sea water background without chemical modification

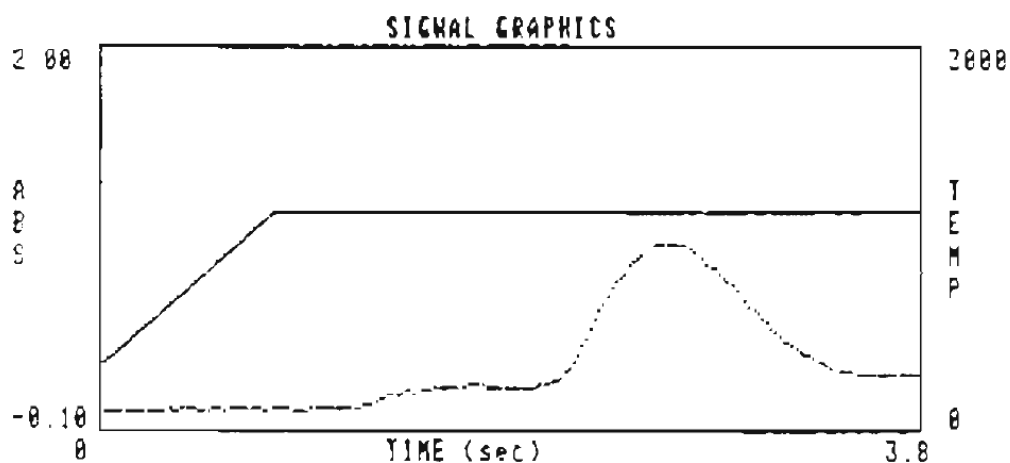


Figure 36. Sea water background with chemical modification

In Figure 35, the large background signal from the atomization of a 5 microlitre sea water sample without matrix modification is shown.

Clearly, at over 4 absorbance units, this background signal could not be corrected properly.

Figure 36 shows that the addition of the chemical modifier to the sea water resulted in a drastic reduction in background signal. This reduction in background signal permitted proper background correction. The reduction in background signal was chiefly due to the action of nitric acid in the chemical modifier, the sodium being volatilized as the nitrate.

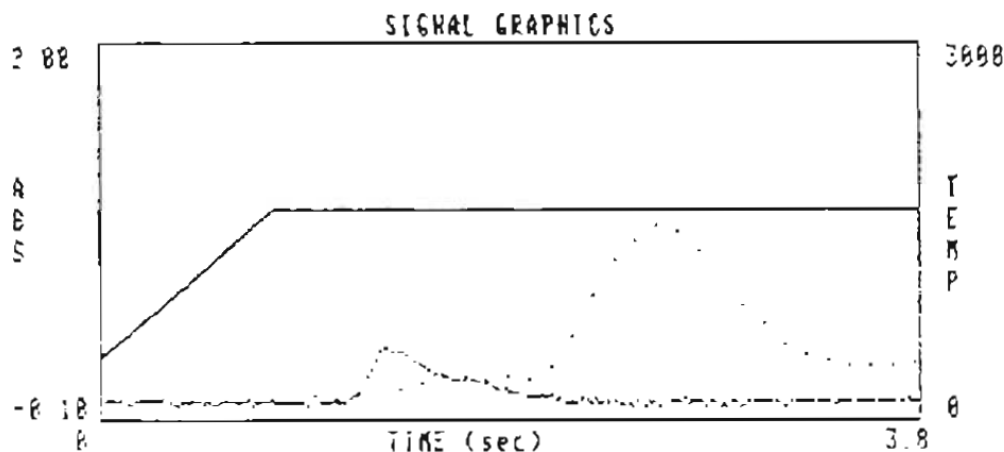


Figure 37. Standard additions signal for cadmium in sea water (platform atomization)

An investigation of ashing temperature showed that the modified sea water sample could be ashed at 500 °C with no significant Cd loss. The analyte stability was due to the ammonium dihydrogen phosphate present in the chemical modifier. The signal graphics allow the operator to study the variation with ashing temperature of both the atomic and background signals simultaneously.

Figure 37 shows a standard additions signal for cadmium in sea water. With the modifier added the major background peak was shifted away from the atomization peak for cadmium. The background signal is shown as a dotted line. The atomic as a solid line. The addition of 10 μL of the mixed modifier proved satisfactory for 10 μL of sea water and would probably be suitable for higher volumes. If necessary the solution can be diluted.

Careful insertion of the platform, alignment of the sampler lip and the light source alignment are all important. Solutions must be placed exactly on the platform to avoid spill over or contact with the sides of the tube. For these reasons wall atomization may be preferred for many analyses.

Cadmium in seawater may be determined directly with wall atomization.

The sample dispenser was programmed to add 40 μL of 2% ammonium oxalate modifier to a 5 μL sea water sample. The standard additions method of calibration is used.

The ammonium oxalate modifier separates the cadmium atomic peak from the background signal. The cadmium is atomized at only 1500 °C and the background is removed with a step to 2000 °C. The modifier does not increase the maximum permissible ashing temperature for cadmium, therefore the sample is ashed at 300 °C. These results indicated that the use of a pyrolytic platform was not necessary for this analysis.

A further improvement to the technique can be obtained if the APDC/MIBK extraction used to clean up reagents of cadmium contamination is used to extract and concentrate the cadmium from sea water. (Refer to methods for sea water)

The method for APDC/MIBK extraction may be modified slightly by adding cyclohexane to the MIBK in the ratio 1:4. This decreases the solubility of MIBK in water and is particularly necessary when large concentration factors are required. This technique was employed on a sea water sample using a 100 fold concentration factor. This produced a 0.5 absorbance atomic signal with negligible background.

Analytical Examples

A study of the suppression of interferences in the measurement of lead in natural and drinking waters has been carried out (369). The effects of a number of salts including sodium chloride, potassium chloride, magnesium chloride and sodium sulphate, were considered. The most severe interferences were experienced for magnesium chloride and sodium sulphate matrices. With the addition of 0.05% lanthanum and 1% nitric acid, the authors successfully reduced the sulphate and chloride interferences, respectively.

A round robin for fourteen metals in water was conducted by the American Society of Testing and Materials (ASTM) to determine whether graphite furnace methods could be included as ASTM standard methods for water testing. Twenty-one American laboratories, including Varian's Atomic Absorption Resource Center (AARC), participated in the determination of the unknown element levels in the supplied samples. Using the GTA-95 graphite tube atomizer with programmable sample dispenser, the results of Schrader et al (370) of the AARC laboratory, were significantly better than the pooled results of all participants. Further, all of the results obtained were within EPA specifications of acceptability when compared to the ASTM expected values released after the study was completed.

In a separate study (371) the same workers investigated the determination of seven priority elements regulated by the US EPA in drinking water and effluent samples. The elements As, Ba, Cd, Cr, Pb, Se and Ag were measured using the GTA-95 graphite tube atomizer. Quantitative recoveries were obtained and the precision was excellent, even when low sample volumes were dispensed. A quality control sample from the ASTM round robin was evaluated, proving the accuracy of the determinations.

The regulations and methodology required by the US EPA for the measurement of priority pollutant metals in drinking waters and effluents were discussed by Volh (372). In this paper, current and imminent legislation and deadlines for compliance to regulations were discussed in detail. Allowable levels of elements under the Primary and Secondary Drinking Water Standards were tabled along with levels of element concentrations above which waste is considered hazardous. The four categories of metal determination – dissolved, suspended, total and extractable, were defined and the sample preparation necessary to measure these quantities was discussed.

An important paper describes a technique for aluminium speciation in natural waters, employing the GTA-95 graphite tube atomizer (373).

Falling pH and increasing aluminium levels have been associated with fish mortality. with dead or moribund fish exhibiting aluminium precipitation in suffocating quantities in the gills. Methods were presented for the determination of total reactive, inorganic monomeric, amorphous, and polymeric aluminium species. Precision, even after the complex extractions, was typically less than 4%, and results for the individual species were in good agreement with those theoretically expected.

Several methods for water analysis using Zeeman background correction were presented in recent work (374).

Solid residues after sample evaporation and also organic chelate extracts were analyzed for a range of elements. After concentrating a water sample on an ion-exchange resin the authors chose to analyze solid samples of the resin by graphite furnace AA. Homogeneity of the solid sample was an important factor with this technique, and background levels were reduced with sample ashing.

The determination of manganese in sea water was examined with Zeeman background correction using a platform technique (375). Results were presented relating the intercalation of sodium chloride in the graphite layers of the tube to tube failure. Other workers determined cadmium levels in coastal sea water (376), testing mono and di-basic ammonium phosphate with nitric acid as matrix modifiers.

Recently, (377) total chromium levels in sea water using Zeeman background correction were determined. The chromium was extracted by passing the sea water sample through a column of diphenylcarbazone slurry coated on silica, with subsequent elution using 0.2 N nitric acid.

In the determination of cadmium using Zeeman background correction, ashing temperatures up to 900 °C were achieved using magnesium nitrate and ammonium phosphate as a matrix modifier (378). An increase in ashing temperature was claimed it small amounts of sodium chloride were mixed with ammonium phosphate.

The mechanism of chloride interferences in graphite furnace AA has been discussed (379). Analyte loss can be attributed to the formation of high bond-energy metal halides, which cannot absorb source light.

Several trace metals in sea water were determined using Zeeman background correction (310). Multiple injection techniques were necessary in most cases, and the authors experienced contamination problems in the determination of manganese. For the determination of nickel peak height measurement proved more effective than peak area measurement.

In a recently published paper a survey of applications using Zeeman background correction, cited references for sea water, natural and waste waters (380). A table of analytical conditions was presented for many elements, however some of the data was incomplete.

Appendix 1 References

| Field | Waters |
|-------------------|--|
| Sample Matrix | Sea Water |
| Key Element | Cd |
| Reagents Required | Ammonium pyrolidine dithiocarbonate (APDC) Methylisobutylketone (MIBK) or Di-isobutylketone (DIBK) Dilute hydrochloric acid Ammonium dihydrogen phosphate Nitric acid (high purity) |

Sample Preparation

Sea Water Sample

Use the programmable sample dispenser to add 10 microlitres of the mixed chemical modifier directly to the sea water sample and any standard additions.

Ammonium Dihydrogen Phosphate Clean Up — Removal of Cadmium Contamination

Prepare a solution of 2 g of ammonium dihydrogen phosphate in 100 mL of deionized distilled water. Adjust the pH of the solution to between 1 and 6 with dilute hydrochloric acid.

Prepare a 1% APDC solution in deionized distilled water. This reagent should be prepared fresh daily.

Mix 5 ml of the APDC solution with the 100 mL of ammonium dihydrogen phosphate solution. Shake the solution for two minutes with 10 mL of MIBK in a separating funnel (di-isobutylketone is also a suitable extraction reagent and has a lower solubility in water than MIBK). Withdraw the aqueous layer and discard the organic layer. The extraction process is repeated twice more.

The purified 2% solution of ammonium dihydrogen phosphate is then combined with the nitric acid in the volume ratio 70:30. Store the modifier in a clean polyethylene container.

Standard Preparation

Prepare suitable aqueous cadmium nitrate standards in 0.1 to 0.5% nitric acid and make up to volume with deionized distilled water.

Calibration Procedure

This procedure uses the pyrolytic platform and plateau tube for the determination of cadmium in sea water.

Use the standard additions technique and employ the programmable sample dispenser to assemble the additions.

The dispenser can assemble all additions by combining volumes from the standard, blank, modifier and sample. At least two additions are necessary.

If normal calibration is attempted, the validity of the normal calibration must be tested against the standard additions calibration. If the gradients of the two lines differ greatly, the normal calibration must not be used. The use of normal calibration may require matrix matching of the

standards to the sample by adding 2 to 3% sodium chloride to the standards.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cd | | Furnace Operating Conditions | | | |
|----------------|------------|------------------------------|----------|----------|------------------------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 200 | 10 | 3.0 | Argon | Dry stage |
| 2 | 200 | 120 | 3.0 | Argon | |
| 3 | 500 | 10 | 3.0 | Argon | Ash stage |
| 4 | 500 | 60 | 3.0 | Argon | |
| 5 | 500 | 2 | 0 | Argon | Gas stop |
| 6 | 1700 | 0.8 | 0 | Argon | Atomize stage |
| 7 | 1700 | 3 | 0 | Argon | |
| 8 | 1700 | 2 | 3.0 | Argon | Tube clean |
| 9 | 40 | 9.8 | 3.0 | Argon | Cool down stage for platform |

Read Command: Steps 6 to 7

Ramp Step: 6. Enter 0 for Maximum Ramp (2000 °C/s)

Furnace Operating Notes

The following sampler parameters were used to prepare the standard additions series.

| Sampler Parameters | Standard Additions | | | |
|--------------------|--------------------|--------|-------|----------|
| | Volumes (µL) | | | |
| Solution | Standard | Sample | Blank | Modifier |
| Blank | — | | 25 | 10 |
| Addition 1 | 5 | 5 | 15 | 10 |
| Addition 2 | 10 | 5 | 10 | 10 |
| Addition 3 | 15 | 5 | 5 | 10 |
| Sample | — | 5 | 20 | 10 |

Recalibration Rate 0

Multiple Injet No Hot Injet No Pre Injet Mod No

The cadmium standard concentration selected would depend on the level of cadmium expected in the sea water.

In open ocean waters cadmium levels can be extremely low. To measure very low concentrations of cadmium, multiple injections of the sample may be necessary and this is achieved automatically by the programmable sample dispenser. For extremely low cadmium concentrations extraction of the cadmium may be necessary. The APDC/MIBK (or DIBK) extraction can be used.

| Field | Waters |
|-------------------|---|
| Sample Matrix | Sea Water |
| Key Element | Cd |
| Reagents Required | Aqueous solution of 2% ammonium oxalate as modifier |

Sample Preparation

Sea Water Sample

The sea water sample was used without any preparation. Ammonium Oxalate Clean Up — Removal of Cadmium Contamination

Cadmium contamination of the ammonium oxalate was found to be insignificant. If the reagent is contaminated the APDC extraction procedure in the previous method should be used.

Standard Preparation

Prepare suitable aqueous cadmium nitrate standards in 0.1% nitric acid and make to volume with deionized distilled water. The concentration level used for this study was 3.2 ng/mL.

Calibration Procedure

This method uses wall atomization with the partitioned pyrolytic graphite tube for the determination of cadmium in sea water.

The standard additions method of calibration is used. The sample dispenser is programmed to add 40 μL of ammonium oxalate modifier directly to a 5 μL sea water sample and standard additions. In this work, 4 and 8 μL of standard were added.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cd | | | Furnace Operating Conditions | | |
|----------------|------------------------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. ($^{\circ}\text{C}$) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 60 | 3.0 | Argon | |
| 3 | 120 | 20 | 3.0 | Argon | |
| 4 | 300 | 30 | 3.0 | Argon | Ash stage |
| 5 | 300 | 10 | 3.0 | Argon | |
| 6 | 300 | 1 | 0 | Argon | Gas stop |
| 7 | 1500 | 1 | 0 | Argon | Atomize stage |
| 8 | 1500 | 1 | 0 | Argon | |
| 9 | 2000 | 5 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 $^{\circ}\text{C}/\text{s}$)

Appendix 1 References

| Field | Waters |
|--------------------|--|
| Sample Matrix | Sea Water |
| Key Element | Cu |
| Also Applicable to | Fe, Cu, Mn, Pb, Ni, Co, Cr |
| Reagents Required | Ammonium Nitrate (AR) (2-10% w/v) as modifier Ammonium Pyrrolidine Dithiocarbamate (APDC) Di-isobutylketone (DIBK) |

Sample Preparation

Sea Water Sample

The ammonium nitrate (20 μL , of 2-10%) is added directly to a sea water sample (20 μL) by the sampler and atomized.

Ammonium Nitrate Clean Up — Removal of Trace Contaminants

Dissolve 1.5 g of APDC in 100 mL of deionized distilled water and filter through a Whatman 541 filter paper into a flask, then stopper. Add 5 mL of the filtered APDC solution to a 10% ammonium nitrate solution (10 g NH_4NO_3 in 100 mL H_2O) with 30 mL of DIBK and shake vigorously for 3 minutes in a separating funnel; leave to stand to permit separation of the phases. Remove the lower aqueous phase and discard the organic layer. The extraction is repeated twice more. The ammonium nitrate is then ready for use as a modifier. Store the purified reagent in a clean polyethylene container.

Standard Preparation

Prepare suitable concentration copper standards in 0.5% nitric acid from stock solution.

Calibration Procedure

The standard additions method of calibration is used. Two additions are required.

Notes

There is evidence to suggest that NH_4NO_3 causes deterioration to the pyrocoated graphite tube. A solution of 2% NH_4NO_3 has been used on a comparable volume of 50% sea water, giving a substantial number of firings before any loss in sensitivity is detected (272). A 2% solution of ammonium oxalate is also a suitable modifier for sea water.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cu | | | Furnace Operating Conditions | | |
|----------------|------------------------------|------------|------------------------------|----------|-------------------------------|
| Step No. | Temp. ($^{\circ}\text{C}$) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 75 | 5 | 3.0 | Argon | Dry stage |
| 2 | 90 | 120 | 3.0 | Argon | 45 μL total volume |
| 3 | 120 | 10 | 3.0 | Argon | |
| 4 | 1050 | 10 | 3.0 | Argon | Ash stage |
| 5 | 1050 | 20 | 3.0 | Argon | |
| 6 | 1050 | 2 | 0 | Argon | Gas stop |
| 7 | 2350 | 1 | 0 | Argon | Atomize stage |
| 8 | 2350 | 2 | 0 | Argon | |
| 9 | 2350 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 $^{\circ}\text{C}/\text{s}$)

Furnace Operating Notes

The programmable sample dispenser was used to prepare the standard additions series. The following program was used for copper.

| Sampler Parameters | | Standard Additions | | |
|--------------------|----------|--------------------|-------|----------|
| Solution | Standard | Sample | Blank | Modifier |
| Blank | — | | 25 | 20 |
| Addition 1 | 5 | 10 | 10 | 20 |
| Addition 2 | 10 | 10 | 5 | 20 |
| Sample | — | 10 | 15 | 20 |

Recalibration Rate 0

Multiple Injet No Hot Injet No Pre Injet Mod No

Other Elements

The maximum ash temperature will depend upon the element being determined. The maximum ash temperature quoted in Chapter Four should be used as a guide for setting the ash temperature for other elements.

| Field | Waters |
|--|--------------------|
| Sample Matrix | Streams, effluents |
| Key Element | Cd |
| Also Applicable to | Pb |
| Reagents Required | |
| Ammonium dihydrogen phosphate solution, 0.5% w/v (used to chemically modify the cadmium). Trace metal impurities of the modifier may be removed by APDC chelation and MIBK extraction (refer to procedure given for sea waters). | |
| Deionized distilled water. | |

Sample Preparation

Collect samples using approved EPA techniques. Stabilize with nitric acid, adding enough to make the pH of the final solution less than 2. This could typically represent a final concentration of about 1% v/v nitric acid. Filter if necessary.

Standard Preparation

Aqueous standards. Stock standard solution 1000 mg Cd/L in 1 M HNO₃. Dilute to make 2 µg Cd/L.

Calibration Procedure

By standard additions technique. Suggested volumes are 10 µL sample, 2 and 5 µL standard addition volumes, 10 µL modifier solution.

Notes

Excessive background signals may be observed at the cadmium wavelength with some samples. Ensure that the furnace program is carefully selected to minimize background interferences.

Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cd | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 90 | 3.0 | Argon | |
| 3 | 120 | 10 | 3.0 | Argon | |
| 4 | 650 | 20 | 3.0 | Argon | Ash stage |
| 5 | 650 | 30 | 3.0 | Argon | |
| 6 | 650 | 2 | 0 | Argon | Gas stop |
| 7 | 2500 | 1 | 0 | Argon | Atomize stage |
| 8 | 2500 | 2 | 0 | Argon | |
| 9 | 2500 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)

Other Elements

The maximum ash temperature will depend upon the element being determined. The maximum ash temperature quoted in Chapter Four should be used as a guide for setting the ash temperature for other elements.

Appendix 1 References

| Field | Waters |
|-------------------|--|
| Sample Matrix | Streams, effluents |
| Key Element | Cr |
| Reagents Required | Deionized distilled water Nitric acid |

Sample Preparation

Collect samples using approved EPA techniques. Stabilize with nitric acid, adding enough to make the pH of the final solution less than 2. This could typically represent a final concentration of about 1% v/v nitric acid. Filter if necessary.

Standard Preparation

Aqueous standards. Stock standard solution 1000 mg Cr/L in 1 M HNO₃. Dilute to make 20 µg Cr/L.

Calibration Procedure

By concentration calibration technique. 10 µL of sample, and 2, 5 and 10 µL of standard are usually adequate.

Notes

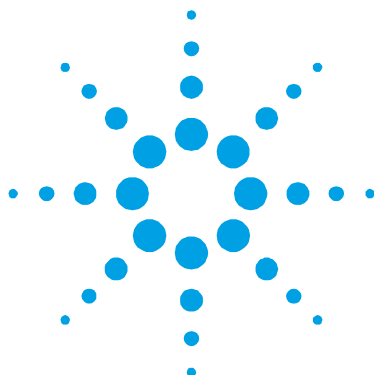
Spectrometer Operating Conditions

Use the instrument operating parameters listed in Chapter Four and check that a typical response is obtained for the element of interest before proceeding with the analysis.

| Key Element Cr | | | Furnace Operating Conditions | | |
|----------------|------------|------------|------------------------------|----------|---------------|
| Step No. | Temp. (°C) | Time (sec) | Gas Flow | Gas Type | Comments |
| 1 | 85 | 5 | 3.0 | Argon | Dry stage |
| 2 | 95 | 60 | 3.0 | Argon | |
| 3 | 120 | 10 | 3.0 | Argon | |
| 4 | 1100 | 20 | 3.0 | Argon | Ash stage |
| 5 | 1100 | 20 | 0 | Argon | |
| 6 | 1100 | 2 | 0 | Argon | Gas stop |
| 7 | 2500 | 0.7 | 0 | Argon | Atomize stage |
| 8 | 2500 | 2 | 0 | Argon | |
| 9 | 2500 | 2 | 3.0 | Argon | Tube clean |

Read Command: Steps 7 to 8

Ramp Step: 7. Enter 0 for Maximum Ramp (2000 °C/s)



8. Chemical Modification Using Reduced Palladium

Introduction

Chemical modification techniques have been widely used in graphite furnace atomic absorption spectroscopy. The ability to maintain the stability of the analyte element at a higher temperature reduces background absorbance and chemical interferences. This can greatly improve the determination of volatile elements in difficult sample matrices. For example, nickel is typically used to stabilize arsenic and selenium to higher temperatures (34, 37). Nickel has also been used for tin, gold, bismuth, and antimony (381).

Palladium can be used to maintain the stability of elements at temperatures several hundred degrees higher than those attained with nickel (382-389). However, the performance of palladium is strongly affected by the sample matrix. For samples containing high concentrations of strong oxidizing agents such as HNO_3 , Na_2SO_4 and H_2SO_4 , palladium alone is a very poor chemical modifier. However, the addition of a reducing agent such as hydroxylamine hydrochloride, ascorbic acid, or 5% hydrogen in the inert gas, provides for more consistent performance of palladium as a modifier. The reducing agent modifies the form of palladium and ensures that palladium is reduced to the metal early in the temperature program.

With proper use of a reduced palladium chemical modifier, ash temperatures for many elements can be increased by an average of 400 °C. Interference performance in high chloride and sulphate matrices is excellent.

Graphics capability is an important facility in methods development. Furthermore, the ability to overlay absorbance signals is extremely valuable in methods development and is an excellent tool for the investigation of the atomization processes.

The development and practical application of chemical modification methods can, of course, be carried out on graphite tube atomizers employing either deuterium background correction or Zeeman background correction. Analysts should note, however, that the background signal displayed may not be the same for both systems. Consequently, 'signal graphics' displays obtained in the analyst's own laboratory for determinations similar to those described in this chapter may not always match the 'signal graphics' examples given here.

Investigations of Chemical Modifiers for Selenium

The overlay of platform atomization peaks of selenium with different modifiers (Ag, Ni, and Pd) is shown in Figure 38. Nickel and palladium stabilized selenium to higher temperatures than did silver and resulted in better sensitivity. Selenium can be stabilized with numerous metals, and studies were carried out using the graphics overlay function to evaluate the usefulness of various modifiers in a variety of sample matrices.

Selenium reacts with many metals and the formation of a more stable selenide species has been used to minimize volatility problems and thus improve graphite furnace analyses.

An empirical investigation of the thermal stability of various metal selenides produced the results listed in Table 16. Copper and cobalt produced results similar to that obtained for nickel. For zinc and silver the usable ash temperature was lower. Both palladium and rhodium permitted significantly higher ash temperatures. The highest ash temperature was attained with molybdenum, but the sensitivity was very poor. It was noted that sensitivity and possible ash temperature were dependent on several conditions. The use of the pyrolytic graphite platform affected the usable ash temperature. Sensitivity and ash temperature were also influenced by the concentration of the modifier, whether the metal was added as a nitrate or chloride salt, and the condition of the graphite tube. Although these results show poorer sensitivity when palladium is used as a modifier, this was not the case when palladium was combined with a reducing agent.

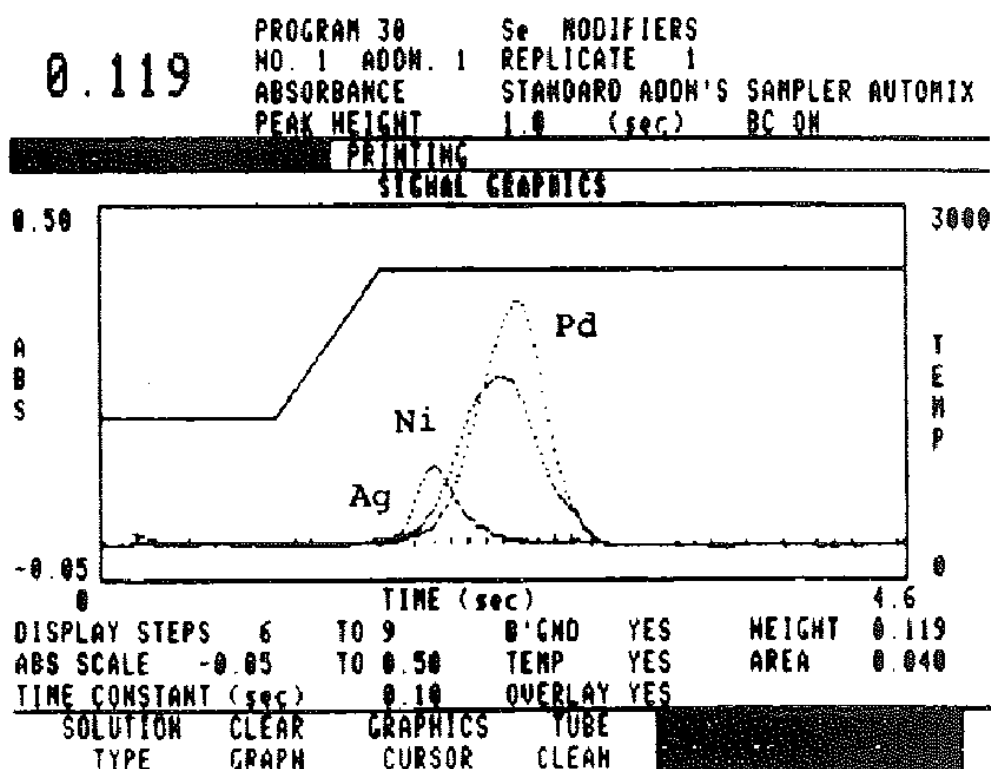


Figure 38. Effect of Ag, Ni and Pd modifiers on selenium platform atomization

Table 16. Selenium modifiers

| Modifier 1000 mg/L | Maximum Ash Temperature (°C) | Relative Sensitivity Peak Height |
|-----------------------|---------------------------------|-------------------------------------|
| Nickel | 700–900 | (1.00) |
| Copper | 800–1000 | 1.00 |
| Cobalt | 800–1000 | 1.09 |
| Zinc | 500–700 | 1.13 |
| Palladium | 900–1100 | 0.70 |
| Rhodium | 1000–1200 | 1.05 |
| Silver | 500–700 | 0.58 |
| Molybdenum | 1200–1400 | 0.24 |

Alternative chemical modifiers for selenium have to be evaluated carefully. Although rhodium and palladium appeared to be excellent modifiers for selenium in high chloride matrices such as sea water, they performed poorly in the Na_2SO_4 matrix. The results of this study are illustrated in Figure 39. The graphite platform was used, and the ash temperatures were optimized for each modifier.

When a reducing agent (hydroxylamine hydrochloride) was added with the palladium, the recoveries of selenium improved to 100% at the levels of Na_2SO_4 used in this study. The main effect of the reducing agent is the reduction of the palladium salt to elemental palladium early in the temperature program. Once reduced, palladium becomes a very effective modifier for selenium in a Na_2SO_4 matrix. It could be assumed that the reducing properties of hot graphite would reduce palladium, but supplementary investigations showed that pre-injecting a palladium solution (no reducing agent) into the graphite tube and heating to 1000 °C was not nearly as effective as chemical reduction. It is possible, therefore, that the reducing agent also influences the atomization process of selenium in ways other than the reduction of palladium.

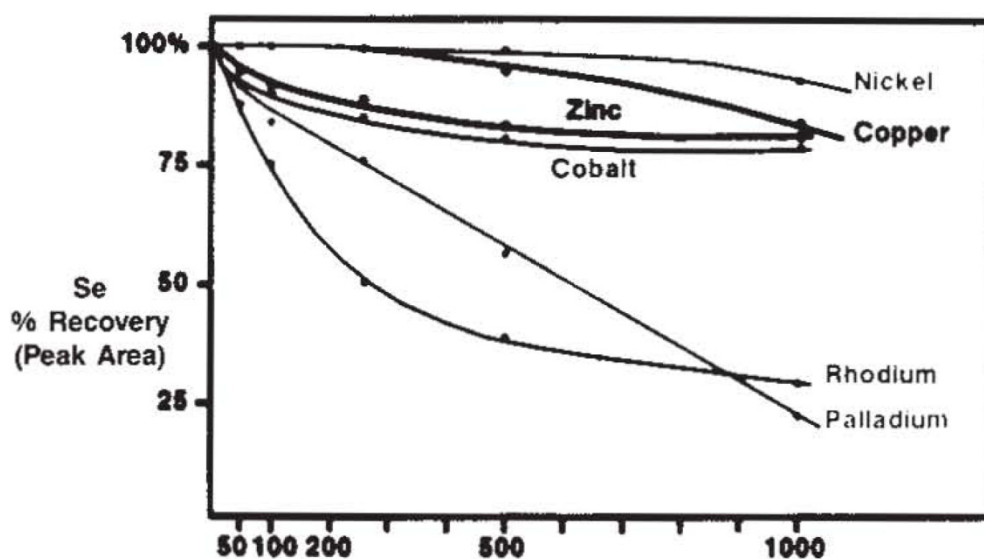


Figure 39. Modifier effectiveness for selenium in Na_2SO_4 matrix

New Chemical Modification Methods

Reduced palladium was investigated as a modifier for many of the elements determined by graphite furnace. Figure 40 illustrates the overlay of lead atomization peaks with and without the modifier. Ash temperature was 450 °C and wall atomization was used. The left-hand atomization peak was obtained from an aqueous lead standard with no chemical modification. The right-hand lead atomization peak was produced with the addition of a mixed modifier of 1000 mg/L Pd, 1% hydroxylamine hydrochloride, and 2.5% hydrochloric acid. When the temperature program was re-optimized, it was found that the ash temperature could be increased to 1000 °C when the modifier was used.

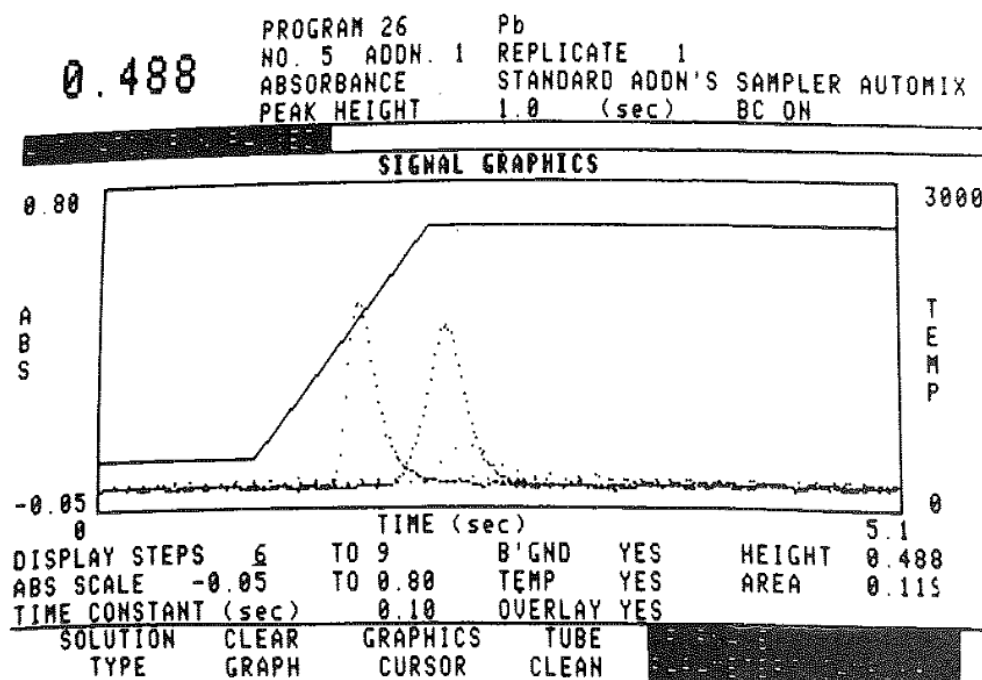


Figure 40. Effect of reduced Pd modifier on Pb atomization

Reduced palladium was an excellent modifier for antimony as illustrated in Figure 41. Not only was there a dramatic shift in peak appearance time, but also, sensitivity improved. The right-hand antimony atomization peak was obtained with a palladium chemical modifier added from two separate solutions (1000 mg/L Pd and 1% ascorbic acid). With the modifier the ash temperature could be increased from 800 °C to 1200 °C.

This chemical modification method can be applied to the graphite furnace determination of many elements. Table 17 lists the increases in ash temperature that are possible. The modifier produces temperature shifts even for the transition metals. Ash temperatures of 1000-1300 °C were possible for most elements investigated in this study. The temperature shift for cadmium was less dramatic. The modifier stabilized mercury to 450 °C with an a times improvement in sensitivity. But the most promising use for this modifier is in the determination of the semimetallic elements (Tl, Sn, Pb, Ge, Sb, As, Bi, Se, and Te). Ash temperatures increased 500-800 °C for these elements. Their determination can be plagued by interference problems and the increased ash temperatures possible with this modifier would be expected to improve their determination in difficult sample matrices.

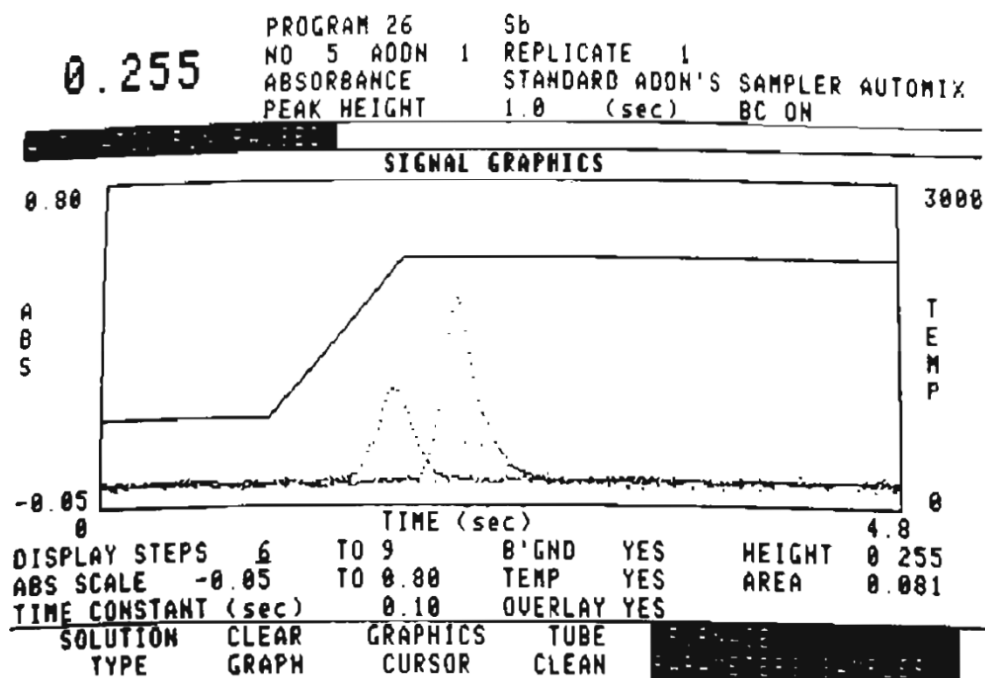


Figure 41. Effect of reduced Pd modifier on Sb atomization

Preliminary Interference Studies

Obviously, before a chemical modifier can be widely used it must be carefully evaluated in a variety of sample matrices. Figure 42 shows the overlay of three 100 $\mu\text{g/L}$ Sb atomization peaks (Sb standard, Sb standard plus 5 μL sea water, and Sb standard plus 5 μL 0.5% Na_2SO_4). Wall atomization was used and the ash temperature was 1400 $^\circ\text{C}$. The recoveries in sea water and 0.5% Na_2SO_4 were 98% and 101% respectively. The modifier was added from two separate solutions (1000 mg/L Pd and 1% ascorbic acid). Identical peak shapes indicate that the atomization process is the same.

A similar experiment was carried out for lead and the results are displayed in Figure 43. Wall atomization was used and the ash temperature was 1000 $^\circ\text{C}$. With the addition of 5 μL sea water, the lead atomization peak was shifted earlier but the recovery was an excellent 96%. The recovery in 0.5% Na_2SO_4 was 80%. A mixed modifier of 1000 mg/l Pd, 1% hydroxylamine hydrochloride, and 2.5% hydrochloric acid was used.

Table 17. Ash temperature with wall atomization

| Element | Recommended Ash Temperature (°C) | Ash Temperature with Pd Modifier (°C) | Change |
|---------|----------------------------------|---------------------------------------|--------|
| Au | 700 | 1100 | +400 |
| Ag | 500 | 950 | +450 |
| Co | 900 | 1200 | +300 |
| Ni | 900 | 1200 | +300 |
| Mn | 800 | 1200 | +400 |
| Fe | 800 | 1300 | +500 |
| Cr | 1100 | 1300 | +200 |
| Cu | 900 | 1100 | +200 |
| Zn | 400 | 900 | +500 |
| Cd | 300 | 550 | +250 |
| Hg | 120 | 450 | +330 |
| Tl | 400 | 1000 | +600 |
| Sn | 800 | 1300 | +500 |
| Pb | 400 | 1000 | +600 |
| Sb | 800 | 1400 | +600 |
| As | 800 (Ni Modifier) | 1500 | +700 |
| Bi | 500 | 1100 | +600 |
| Se | 700 (Ni Modifier) | 1100 | +400 |
| Te | 500 | 1300 | +800 |

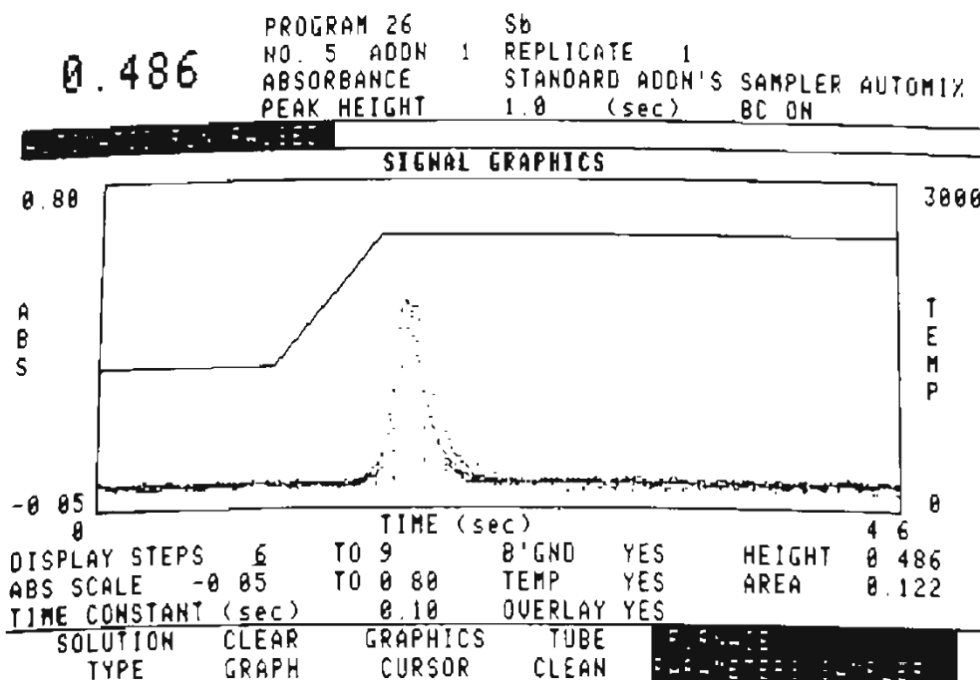


Figure 42. Interference from sea water and Na₂SO₄ matrices on Sb atomization (reduced Pd modifier used)

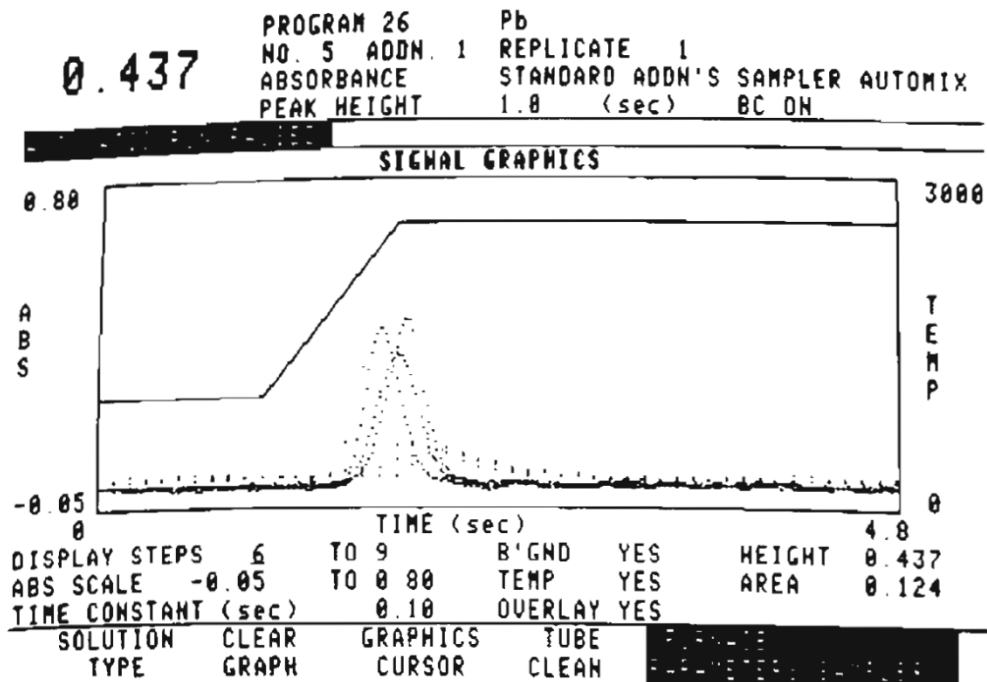


Figure 43. Interference from sea water and Na₂SO₄ matrices on Pb atomization (reduced Pd modifier used)

Results of preliminary interference investigations are listed in Table 18. Most of these results were obtained by injecting directly into the furnace 5 µL of 1000-2000 mg/L Pd as the chloride, 5 µL of 1% ascorbic acid, standard and interferent solutions. For some of the elements, 5-10 µL of a pre-mixed modifier of 2000 mg/L Pd, 2% hydroxylamine hydrochloride, and 2% hydrochloric acid was used. The results listed in Table 18 were obtained with wall atomization and peak height measurements. Recoveries were similar whether wall or platform atomization was used. There appeared to be little advantage with the graphite platform in this study.

Table 18. Preliminary interference performance wall atomization — peak measurement

| Element | Recovery in 5 µL sea water | Recovery in 5 µL 0.5% Na ₂ SO ₄ |
|---------|-------------------------------|--|
| Au | 90% | 93% |
| Ag | 101% | 93% |
| Sb | 99% | 105% |
| Co | 93% | 98% |
| Ni | 98% | 107% |
| Mn | 108% | 112% |
| Cd | 123% | 84% |
| Cr | 109% | 105% |
| As | 94% | 95% |
| Te | 100% | 103% |
| Se | 84% | 83% |
| Sn | 105% | 76% |
| Tl | 90% | 77% |
| Bi | 93% | 76% |

Characteristics of Chemical Reducing Agents

This chemical modification method can be applied to the determination of numerous elements in a variety of sample matrices. The mechanisms are not yet completely understood so that at the time of going to press it is not possible to make firm recommendations about types of reducing agent and concentrations of palladium and reducing agent. It appears that various types of chemical reducing agents can be used, including ascorbic acid, hydroxylamine hydrochloride, hypophosphorous acid, and formic acid. An excellent modifier for tin was 5 μL of 1000-2000 mg/L Pd and 5 μL of 1% ascorbic acid added as separate solutions directly into the graphite furnace with 10 μL of sample. It is often not practical to combine palladium and ascorbic acid in the same solution. Ascorbic acid is a powerful enough reducing agent to precipitate palladium out of solution relatively rapidly. This is also the case for hypophosphorous acid and formic acid. Hydroxylamine hydrochloride can be added to the palladium solution with no precipitation of palladium. A mixed modifier of 2000 mg/L Pd, 2% hydroxylamine hydrochloride and 2% hydrochloric acid was used to determine selenium in a variety of waste water samples with very good results. (5-10 μL of modifier was added to 10-20 μL of sample.) However, hydroxylamine hydrochloride produced poor results for the determination of some other elements (arsenic for example).

Different reducing agents give various degrees of success depending on the element and to some degree the sample matrix. Depending on the reducing agent, palladium is deposited in different physical form and the reducing agent itself may leave deposits on the graphite surface that can affect the atomization process. Scanning electron micrographs showed that when a palladium solution (no reducing agent) is introduced into the graphite furnace, and the graphite tube is heated to 1000 $^{\circ}\text{C}$, palladium forms droplets of various sizes (Figure 44). However, when palladium is introduced with ascorbic acid it is deposited in a much more finely divided form dispersed among flakes of carbon (Figures 45a and 45b). The palladium modifier is very efficient in the presence of organic material that decomposes leaving a carbon residue.

It is believed that reduced palladium becomes a more efficient modifier when it is present on the graphite surface in a finely divided form rather than in droplets. Therefore, ascorbic acid is the recommended reducing agent for most applications. However, for the determination of selenium in a variety of samples, hydroxylamine hydrochloride produced superior results. More investigations are needed to better establish how this chemical modification method should be practiced.

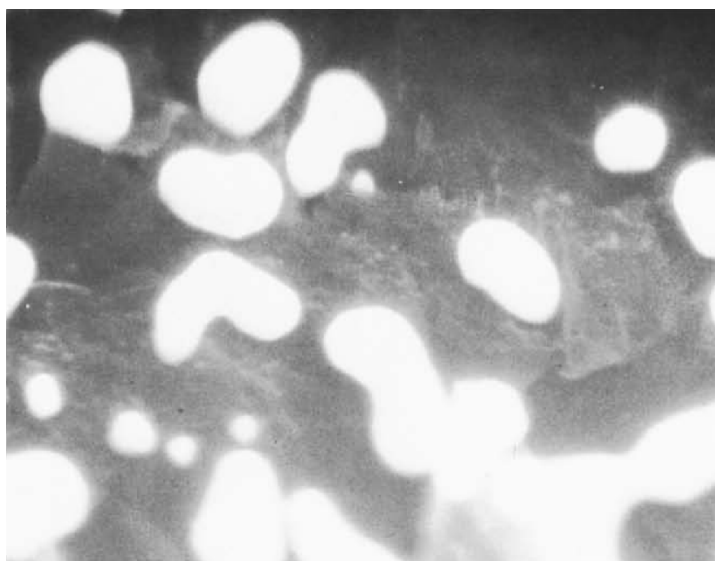


Figure 44. Scanning electron micrograph (20,000 \times ; palladium deposited from dilute aqua regia solution; graphite heated to 1000 $^{\circ}\text{C}$)



Figure 45a. Scanning electron micrograph (2,000×; palladium deposited with ascorbic acid; graphite heated to 1000 °C)

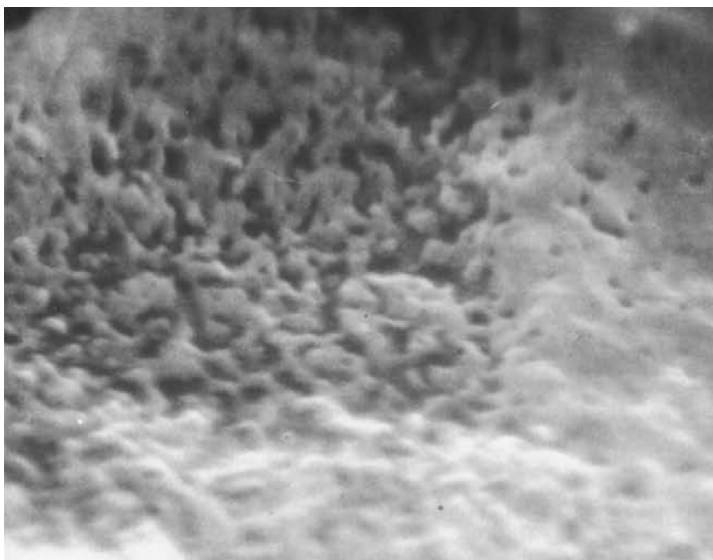


Figure 45b. Scanning electron micrograph (20,000×; palladium deposited with ascorbic acid; graphite heated to 1000 °C)

Some general characteristics of this chemical modification method have been observed for a variety of elements and can be summarized as follows:

- 1 Chloride interference is greatly reduced.
- 2 Excellent results with wall atomization.
- 3 Very efficient modifier for samples with high organic content.
- 4 Sensitive to HIGH concentrations of strong oxidizers.

The chloride interference is greatly reduced and high concentrations of hydrochloric acid can be used. Recoveries in sea water were very good. This modifier delays atomization of the analyte element until a higher gas phase temperature is achieved and thus minimizes the chloride interference. This is, of course, similar to the benefit seen with the graphite platform. With the significantly higher ash temperatures possible with palladium there appears to be little benefit in using the graphite platform. Analyte volatilization is delayed by chemical means rather than by the platform.

Palladium is an excellent modifier when used under reducing conditions. The presence of high concentrations of organics appears to make the conditions in the graphite furnace more reducing and helps to disperse the palladium in a more finely divided form. Palladium used under oxidizing conditions is a severe interferent for many elements. For this reason, the addition of a reducing agent is required for consistent performance. If a sample contains high concentrations of strongly oxidizing species, higher amounts of the reducing agent may be necessary. Chemical reducing agents would be expected to lose their effectiveness in the presence of high concentrations of nitric acid due to the oxidation of the reducing agent. It is generally preferable to use nitric acid at concentrations lower than 5%.

Hydrogen as a Reducing Agent

There are advantages in using hydrogen as the reducing agent. Potential contamination from chemical reducing agents is eliminated and hydrogen leaves no residues that could have detrimental effects on the atomization process. It also simplifies this chemical modification method.

Excellent results were obtained using a mixed gas of 5% hydrogen and 95% argon throughout the temperature program. A chemical modifier of 1500 mg/L Pd and 1% glycerine was used. The results of interference studies are reported in Table 19. Interferent solutions of hydrochloric acid, sodium chloride, sea water, nitric acid, and sodium sulphate were introduced directly into the graphite furnace along with the analyte element solution. Recoveries were calculated by comparing both peak height and peak area absorbances to those obtained from an interferent-free standard. Results were excellent. One advantage of hydrogen over the use of chemical reducing agents is that high concentrations of nitric acid do not appear to affect the reduction of palladium.

The physical form of palladium is still important. It is believed that when only hydrogen is used as a reducing agent the palladium is deposited on the graphite surface as small droplets of various sizes (as shown earlier). It was typical to see irregularly shaped atomization peaks particularly on new pyro-coated graphite tubes for elements such as arsenic and tin. This may be due to uneven release of the analyte element from different sized droplets of palladium. The addition of a small amount of organic material greatly improves the peak shapes and the results when hydrogen is used. Glycerine was added to the palladium solution to contribute carbon and influence the physical form of the deposited palladium (produce a more finely divided form).

The condition of the graphite surface also influences the way in which the palladium is deposited and directly affects the efficiency of the modifier. The pyrolytic-coated graphite tubes used to obtain the results in Table 19 had already been used for more than 100 injections. Recoveries were poorer on new pyrolytic-coated graphite tubes. Again, it is believed that the physical form of palladium is the key. Palladium would be expected to form large droplets on the relatively smooth and unreactive surface of a new pyrolytic-coated graphite tube as distinct from the way in which deposition occurs on the 'roughened' surface of a used graphite tube.

This chemical modification method produced excellent results on uncoated graphite tubes. The same chemical modifier of 1500 mg/L Pd and 1% glycerine was used. The results of interference studies for thallium and arsenic on an uncoated tube are reported in Table 19. After an uncoated tube was conditioned with 5-10 injections of the modifier solution, the absorbance signals remained consistent for several hundred injections. Figures 46a and 46b (peaks from the interference studies) show the similarity of thallium atomization signals on pyrolytic-coated and uncoated graphite tubes. Peak shapes and appearance lines are reproducible even in the presence of high concentrations of HCl, NaCl, HNO₃, and Na₂SO₄.

Table 19. Results of Interference Studies

| Element | Sensitivity | Interferent Solution | | | | |
|-----------------|-------------|-----------------------|----------------------|-----------------------------------|------------------------------------|---|
| | | 5 μ L Conc HCl | 5 μ L 5% NaCl | 5 μ L Sea H ₂ O | 5 μ L Conc HNO ₃ | 5 μ L 1% Na ₂ SO ₄ |
| Thallium | | | | | | |
| coated tube | 12 pg | 99% (H) | 89% | 103% | 98% | 86% |
| 900 °C ash | | 101% (A) | 93% | 100% | 103% | 89% |
| 2600 °C atomize | | | | | | |
| uncoated tube | 16 pg | 102% (H) | 100% | 104% | 95% | 82% |
| 1000 °C ash | | 104% (A) | 100% | 95% | 102% | 94% |
| 2600 °C atomize | | | | | | |
| Arsenic | | | | | | |
| coated tube | 12 pg | 100% (H) | 95% | 99% | 108% | 104% |
| 1300 °C ash | | 100% (A) | 106% | 97% | 105% | 100% |
| 2700 °C atomize | | | | | | |
| uncoated tube | 12 pg | 97% (H) | 93% | 98% | 86% | 99% |
| 1300 °C ash | | 98% (A) | 96% | 93% | 74% | 98% |
| 2700 °C atomize | | | | | | |
| Lead | | | | | | |
| coated tube | 4 pg | 98% (H) | 89% | 96% | 98% | 89% |
| 1000 °C ash | | 96% (A) | 101% | 105% | 102% | 95% |
| 2600 °C atomize | | | | | | |
| Tin | | | | | | |
| coated tube | 9 pg | 103% (H) | 89% | 70% | 100% | 97% |
| 1300 °C ash | | 98% (A) | 96% | 78% | 97% | 100% |
| 2700 °C atomize | | | | | | |

coated tube = pyrolytic coated graphite tube atomizer

(H) = peak height measurement

(A) = peak area measurement

The atomization signals of lead from the interference studies are illustrated in Figure 47. The results are reported in Table 19. A pyrolytic-coated graphite tube was used. The temperature program used for lead in the interference studies is shown in Figure 48. A mixed gas of 5% hydrogen and 95% argon was used throughout the temperature program. The dry portion of the temperature program (steps 1-4) was relatively long to allow time for the hydrogen to react with the palladium.

Atomization temperatures were typically 2500-2700 °C. For some elements such as tin and arsenic, it appears that the analyte element is not efficiently released until the palladium volatilizes. Therefore rapid heating to a high atomization temperature is required.

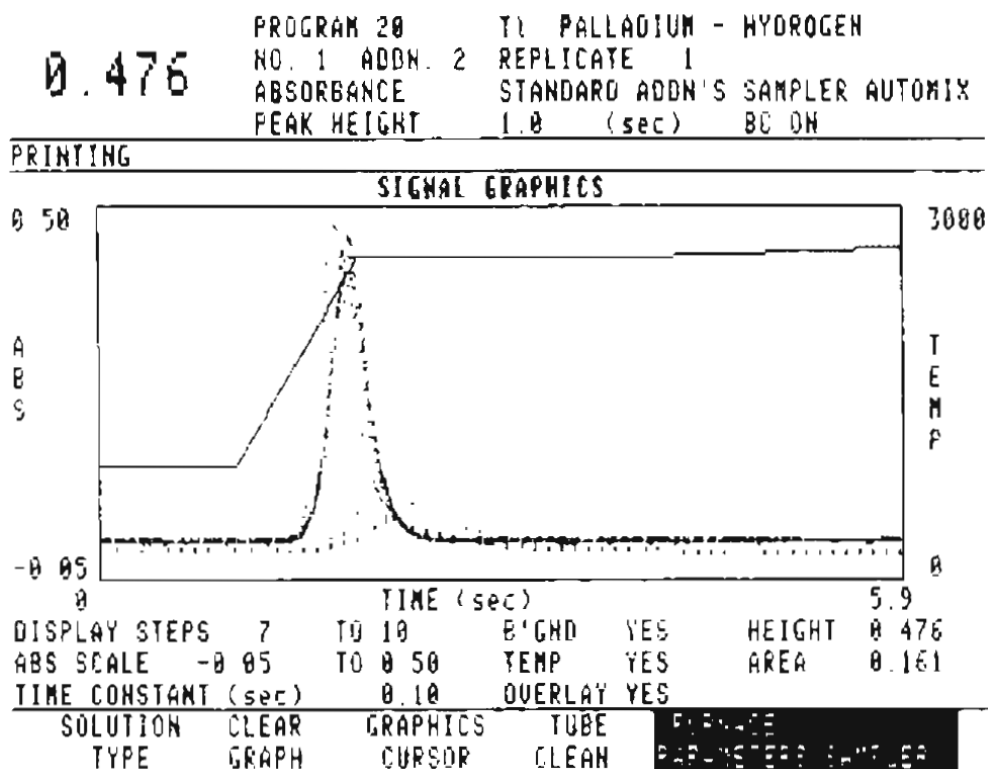


Figure 46a. Interference study 1 ng thallium pyrolytic coated graphite

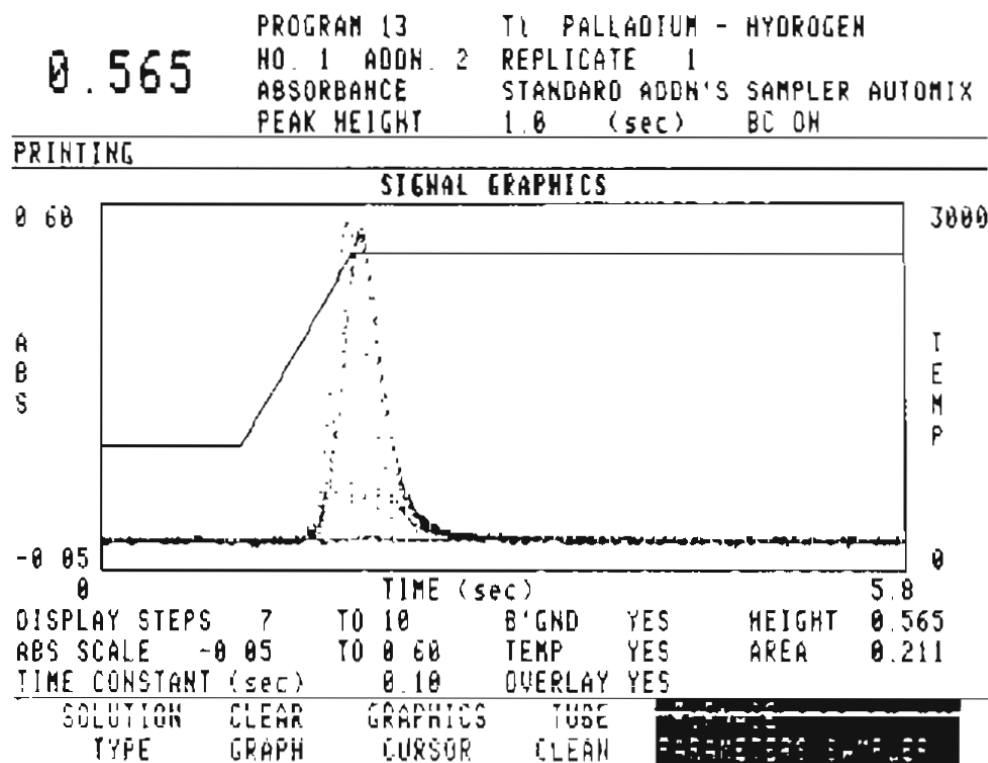


Figure 46b. Interference study 2 ng thallium uncoated graphite

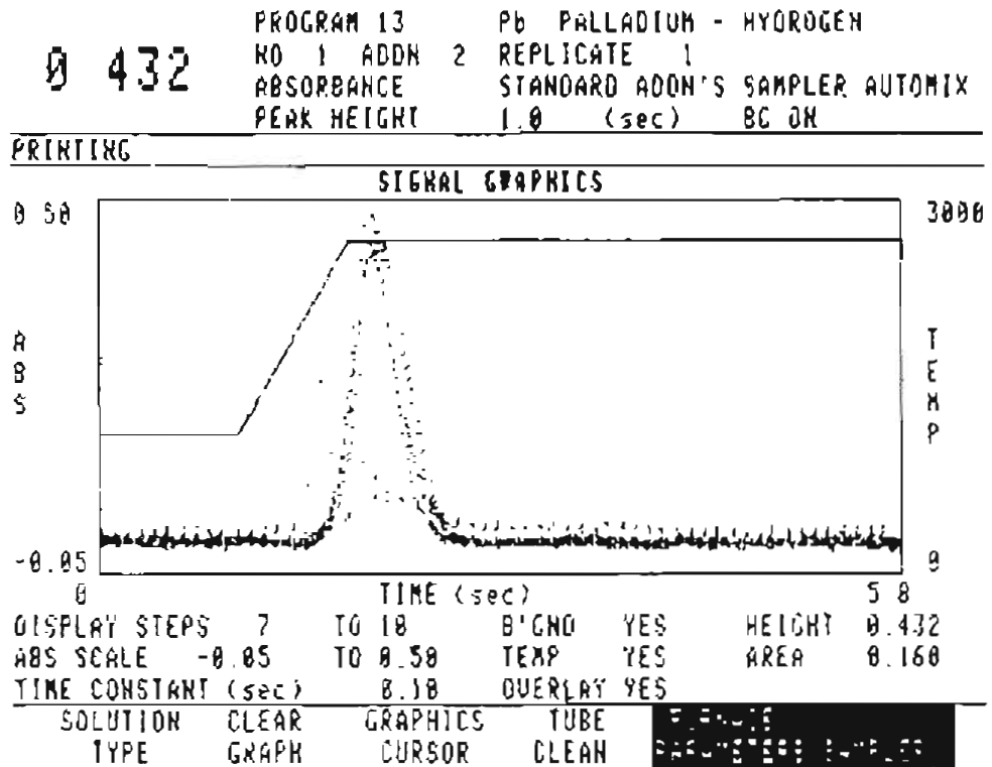


Figure 47. Interference study lead atomization signals

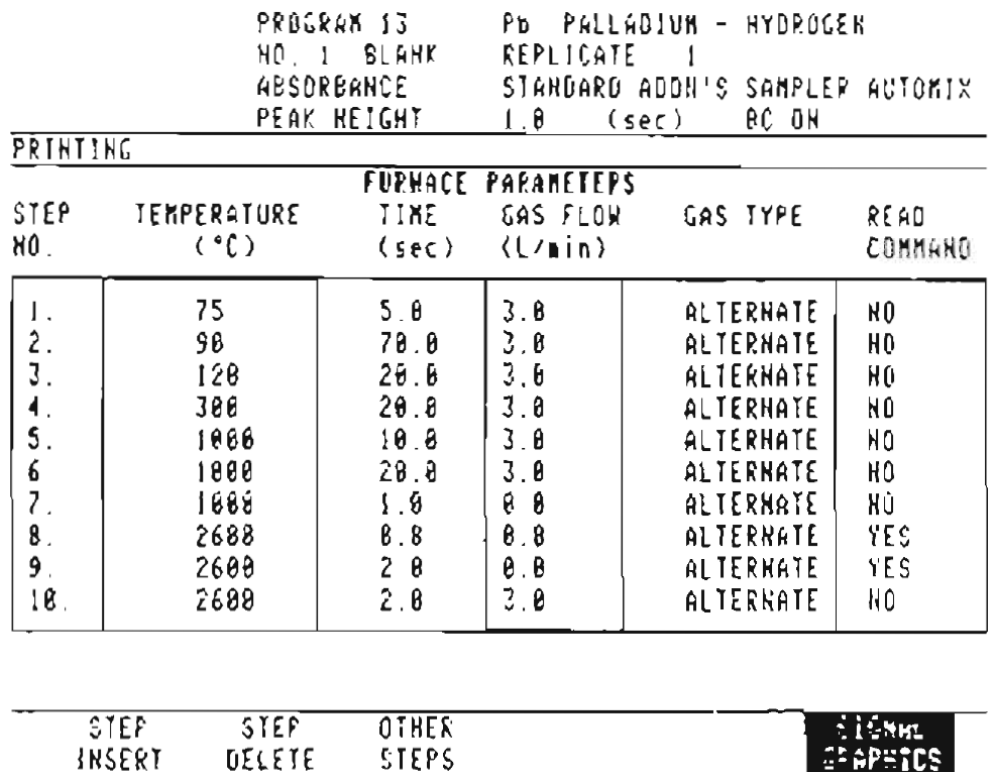
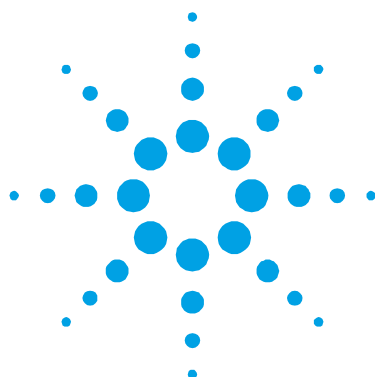


Figure 48. Lead temperature program

Summary

Reduced palladium is an excellent modifier for graphite furnace atomic absorption. It can be used to improve many of the more difficult analyses. It promises to be a more universal modifier. Determinations for a variety of elements in different matrices show similar characteristics indicating a similar atomization process regardless of sample matrix. Interferences are thus reduced and follow a more predictable pattern. This of course has very good implications for the improvement of graphite furnace techniques.



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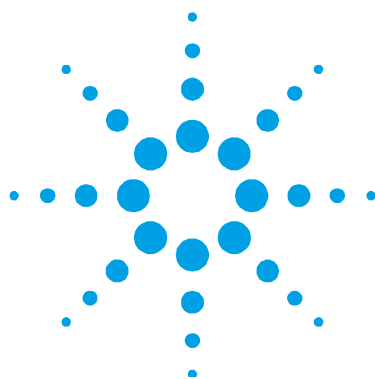
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Appendix 2 Explanation of Some Terms

Accuracy

The closeness of the measured value to the true value. The accuracy of a measurement is therefore dependent on the care with which the chemist prepares known standards and sample solutions for the analysis. Interference effects also can affect the accuracy of a measurement.

Precision

The reproducibility of a series of measurements. Often expressed as R.S.D.%. The precision is affected by the manner in which the absorbance measurements are taken. In graphite furnace AA, the precision can be influenced by the care taken in injecting the solutions, and by the selection of the correct program parameters.

Interference

An interference in furnace AA is any effect whether chemical or physical which changes the measured absorbance obtained for a given amount of the analyte.

Interference effects can be positive or negative in their magnitude, and often occur when the analyte is present in a complex sample matrix (see also Chapters One and Three).

Chemical Modifier

A chemical modifier is a reagent which when added to the sample either reduces interference, or isolates the analyte in a specific form that allows separation between background and analyte atomic absorption signals. An ideal chemical modifier is a reagent that performs both of these functions (see also Chapter One). A chemical modifier could be considered as producing a controlled chemical interference effect which has desirable benefits from the analytical viewpoint.

Standard Deviation (δ)

Where:

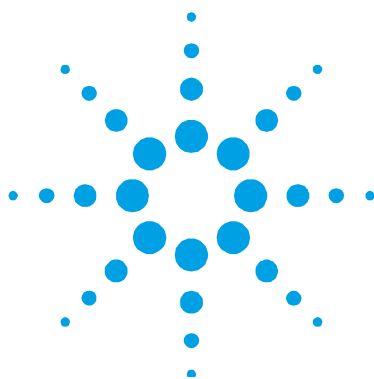
$$\delta = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{N - 1}}$$

\bar{x} is the mean of a series of determinations: $\frac{\sum x_i}{N}$

x_i is each individual measurement

N is the number of measurements

$$\text{RSD} = \frac{\delta \times 100\%}{\bar{x}}$$



Appendix 3 Suppliers of Solutions and Reagents

Standard Metal Solutions and Reagents

J.T. Baker Chemical Co.,
222 Red School Lane,
PHILLIPSBURG, N.J. 08865, U.S.A.

BDH Chemicals Ltd.,
POOLE, Dorset BH12 4NN,
England, U.K.

Carlo Erba,
Divisione Chimica Industriale,
Via C. Imbonati 24, 20159
MILANO., Italy.

Harleco,
Div. of American Hospital Supply Corp.,
60th and Woodland Avenues,
PHILADELPHIA, Pa, 19143, U.S.A.

Hopkin & Williams Ltd.,
P.O. Box 1,
ROMFORD, Essex RM1 1HA,
England, U.K.

Johnson Matthey Chemicals Ltd.,
74 Hatton Garden,
LONDON EC1P 1AE,
England, U.K.

May & Baker Ltd.,
DAGEN HAM, Essex RM10 7XS,
England, U.K.

E. Merck, D 61,
DARMSTADT,
West Germany.

ALFA Division,
Ventron Corp.,
152 Andover Street,
DANVERS, Mass. 01923, U.S.A.

Organometallic Standards

Conastan Div.,
Continental Oil Co.,
P.O. Drawer 1267,
PONCA CITY, Okla., 7460, U.S.A.

Eastman Organic Chemicals,
Eastman Kodak Co.,
343 Slate Street,
ROCHESTER, N.Y., 14650, U.S.A.

Division of Chemical Standards,
National Physical Laboratory,
TEDDINGTON, Middlesex, TW11 0LW,
England, U.K.

National Spectrographic Laboratories Inc.,
19500 South Miles Road,
CLEVELAND, Ohio, 44128, U.S.A.

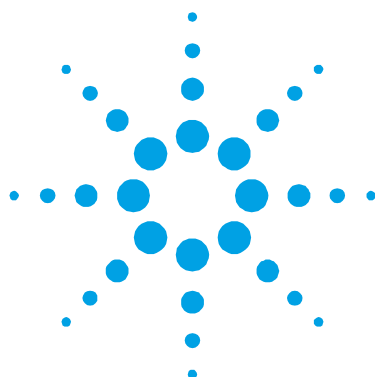
Reference Materials

Bureau of Analysed Samples Ltd ,
Newham Hall,
NEWBY, Middlesbrough, Cleveland T88 9EA,
England, U.K.

U.S. Department of Commerce,
Office of Standard Reference Materials,
Room 8311, Chemistry Building,
National Bureau of Standards,
WASHINGTON, DC. 20234, U.S.A.

Commission of European Communities,
Community Bureau of Reference (BCR),
200 Rue de la Loi,
B-1049 Brussels,
BELGIUM.

National Physical Laboratory,
Office of Reference Materials,
Teddington,
Middlesex, TW1 0LW
England, UK



Appendix 4 Some Recommended Text Books

Electrothermal Atomization for Atomic Absorption Spectrometry,
C.W. Fuller,
Analytical Sciences Monograph No.4,
Chemical Society, London, 1977.
ISBN 0583-8894

Spectrochemical Analysis by Atomic Absorption,
W.J. Price, Heyden & Son Ltd., 1979.
ISBN 085501 455 5

Annual Reports on Analytical Atomic Spectroscopy,
Volumes 1-12, The Chemical Society,
Burlington House, London, WIVOBN, England, (1971-1982).

A Handbook of Decomposition Methods in Analytical Chemistry,
Prof. Rudolf Bock & Dr. Iain L. Marr,
International Textbook Company Ltd.,
(Blackie Group),
Edinburgh and Glasgow, UK.
ISBN 07002 02692

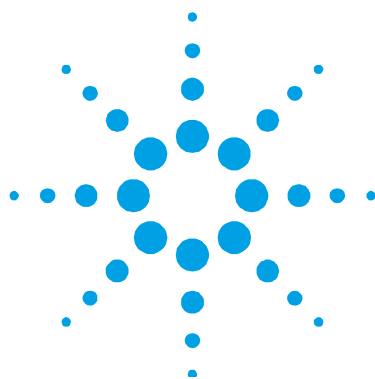
Analytical Absorption Spectroscopy, Selected Methods,
Jon C. Van Loon,
Academic Press, New York, U.S.A. (1980).
ISBN 0-12-714050-6

Toxic Metals and Their Analysis,
Elanor Berman,
Heyden and Son Ltd., 1980.
ISBN 0 85501 468 7

Atomic Absorption Spectrochemical Analysis,
BV L:Vov,
Adam Hilger Ltd., London, (1970).
ISBN 0 85274 109 x

Spectrochimica Acta Part B (Special Issue),
Volume 39B. Numbers 2/3. 1984.
Pergamon Press.

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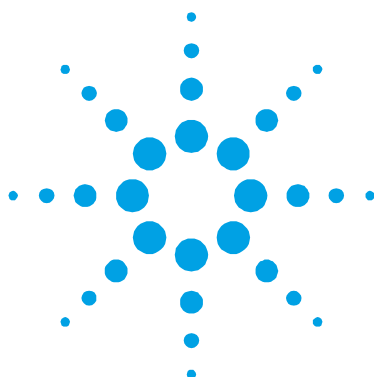
Appendix 5 Other Publications on Specific Methods

Techniques of Water Resources Investigations of the United States Geological Survey, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Book 5, Chapter A 1, Laboratory Analysis, M.W. Skaigstad, M.J. Fishman, L.C. Friedman, D.E. Erdmann and S.S. Duncan, Editors, U.S. Government Printing Office, Washington D.C., U.S.A. Publication stock number 024-001-03177-9,

APHA Standard Methods for the Examination of Water and Waste Water, American Public Health Association Inc., 1015, Fifteenth Street, N.W., Washington D.C. 20005, U.S.A

Methods for Metals in Drinking Water (1978) and Methods for Chemical Analysis of Water and Wastes (1979), U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, U.S.A.

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Appendix 6 Other Publications on Specific Methods

U.S. Government Printing Office (Federal Register),
The Superintendent of Documents,
U.S. Government Printing Office,
WASHINGTON, D.C. 20402., U.S.A.

Association of Official Analytical Chemists,
(J. Assoc. Off. Anal. Chem.),
1111 N. 19th Street. Suite 210R,
Arlington, VA 22209, U.S.A.

National Institute for Occupational Safety and Health,
Division of Surveillance, Hazard Evaluation and Field Studies,
Division of Physical Sciences and Engineering,
4676 Columbia Parkway,
CINCINNATI, Ohio, 45226, U.S.A.

Occupational Safety and Health Administration Analytical Laboratory,
390 Wakara Way,
SALT LAKE CITY, Utah, 84108, U.S.A.

American Society for Testing and Materials (ASTM),
1916 Race Street,
PHILADELPHIA, Pennsylvania, 19103. U.S.A.

Food and Drug Administration (FDA),
WASHINGTON, D.C. 20204, U.S.A.

U.S. Geological Survey,
Water Resources Division,
5293 Ward Road,
ARVADA, Colorado, 80002. U.S.A.

U.S. Environmental Protection Agency,
Office of Research and Development,
Environmental Monitoring Systems Laboratory,
Research Triangle Park,
N.C., 27711, U.S.A.

The Royal Society of Chemistry,
Burlington House,
London, W1V 0BN, U.K.

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