

Introduction

ICP-MS equipped with collision/reaction cell is now the standard analytical technique for metallic impurities of materials including environmental samples, food, rocks, drinking water and chemicals. However, spectral interferences still create problems when determining several elements. Dilution or use of the minor isotope was the best choice to avoid such problems, however semiconductor industries in particular require higher detectability of elements in complex but highly pure chemicals. For example, on determination of Ti in  $H_2SO_4$ ,  $^{47}Ti$  is chosen and  $^{46}Ti$  is used for the analysis of  $H_3PO_4$ ; what isotope of Ti should be used for analyzing the mixture of  $H_2SO_4$  and  $H_3PO_4$ ? In the example of phosphorus, P has only one isotope of  $^{31}P$  which is susceptible to common  $HNO_3$  spectral interference. Until now, the use of high resolution ICP-MS was the solution. This poster demonstrates how the new ICP Triple Quadrupole MS (ICP-QQQ) from Agilent can solve these issues.

Experimental

Instrument

The Agilent ICP-QQQ as illustrated in Figure 1 was used, with hydrogen, oxygen and ammonia gases chosen as the reaction cell gas. PFA nebulizer, 2.5 mm injector (quartz or platinum) torch and spray chamber (quartz or PFA) were the sample introduction devices. The sample solution was introduced by self aspiration of the nebulizer. The sampling cone and skimmer cone were made of platinum with nickel. Metallic impurities of all the chemicals used for analysis were guaranteed to be less than 10 0ppt by manufacturers.

Operating Conditions

- RF power: 1600 W
- Sampling depth: 8 mm
- Carrier gas flow rate: 0.8 L/min (Uptake is approx. 200mL/min)
- Makeup gas flow rate: 0.4 L/min
- ORS gas: 100%  $H_2$ , 10%  $NH_3$  balanced with He and 100%  $O_2$
- Purity of ORS gases was higher than 99.995%.

Table 1. BEC of Phosphorus in UPW (0.8%  $HNO_3$ ), ppb

$H_2$	$NH_3$ with $H_2$	$O_2$
$^{31}P / ^{31}PH_3$ 0.07	$^{31}P / ^{31}P^{14}NH_3$ 0.12	$^{31}P / ^{31}P^{16}O$ 0.10
$^{31}P / ^{31}PH_4$ 0.08	$^{31}P / ^{31}P(NH_3)_2$ 0.10	$^{31}P / ^{31}P^{16}O^{16}O$ 0.20
$H_2$ flow rate scc/min 10	$NH_3$ flow rate scc/min 0.5	$O_2$ flow rate scc/min 5
	$H_2$ flow rate scc/min 10	

Q1 was set at mass 31 to introduce  $^{31}P$  and isobaric polyatomic ions, and Q2 was set at different masses to pass only product ions. Addition of hydrogen to the ammonia reaction cell enhanced the production of  $PNH_3$  and  $P(NH_3)_2$  ions.

Results and Discussion

Spectral interference by nitric acid, which is the major problem hampering P detection by conventional ICP-MS, was completely eliminated, as shown in Figure 2.

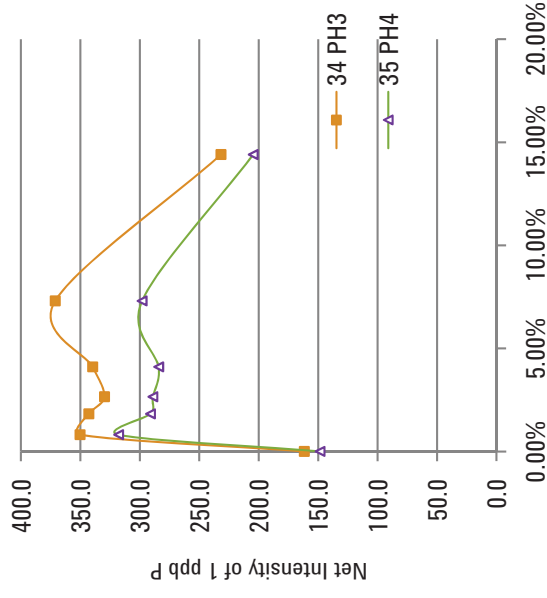


Figure 2. Effect of  $HNO_3$  concentration on P signal

20% Hydrochloric Acid

The major spectral interferences found in Cl- matrices solution are  $^{35}Cl^{16}O$  on  $^{51}V$ ,  $^{35}Cl^{16}OH$  on  $^{52}Cr$ ,  $^{37}Cl^{37}Cl$  on  $^{74}Ge$  and  $^{40}Ar^{35}Cl$  on  $^{75}As$ . BECs and DLs of these elements shown below were obtained from 20% HCl.

	V	Cr	Ge	As
ORS Gas	$NH_3$	$NH_3$	$O_2$	$O_2$
Q1 / Q2	$^{51}V / ^{51}V$	$^{52}Cr / ^{52}Cr(NH_3)_2$	$^{74}Ge / ^{74}Ge^{16}O$	$^{74}Ge / ^{74}GeO_2$ / $^{75}As / ^{75}As^{16}O$
BEC, ppt	0.4	13	4	3
DL, ppt	0.4	8	1.5	2.5

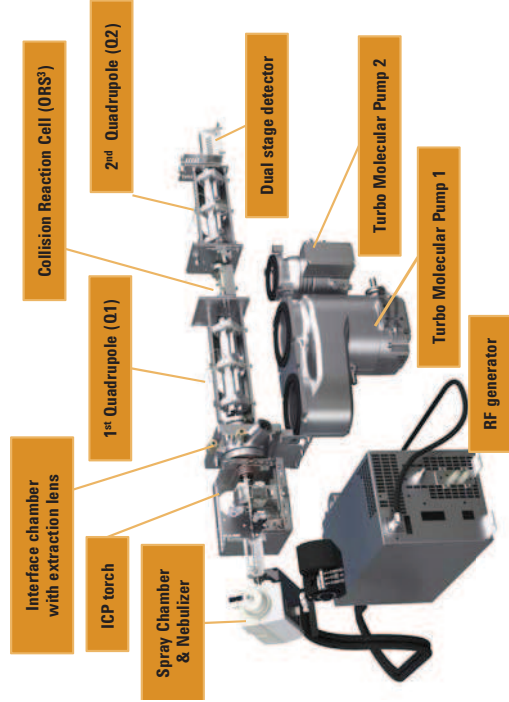


Figure 1. Configuration of Agilent ICP-QQQ

Results and Discussion

**10x Diluted Sulfuric Acid (9.8%)**

BEC of phosphorus obtained from 9.8% H<sub>2</sub>SO<sub>4</sub> by ICP-QQQ reaction mode was compared with that of conventional He collision mode. NH<sub>3</sub>, H<sub>2</sub> and O<sub>2</sub> reaction gases provided similar BECs.

Mode	NH <sub>3</sub>	H <sub>2</sub>	O <sub>2</sub>
01 / O2	<sup>31</sup> P / <sup>31</sup> PNH <sub>3</sub>	<sup>31</sup> P / <sup>31</sup> PH <sub>4</sub>	<sup>31</sup> P / <sup>31</sup> P <sup>16</sup> O
BEC, ppb	0.16	0.15	0.16
7700s He	20 ppb		

H<sub>2</sub>SO<sub>4</sub> is well known to create troublesome polyatomic ions which make it difficult to determine some elements at ppt levels. Spectral interferences of <sup>32</sup>S<sup>16</sup>O on <sup>48</sup>Ti and of <sup>34</sup>S<sup>16</sup>OH on <sup>51</sup>V could be avoided by using NH<sub>3</sub> gas reaction for determination. However, appropriate reactions were not found to create product ions of Cr and Zn. For determination of these elements, He collision is still the best choice to avoid spectral interferences of <sup>36</sup>S<sup>16</sup>O and S<sub>2</sub> ions.

<sup>48</sup> Ti		<sup>51</sup> V		<sup>52</sup> Cr		<sup>68</sup> Zn	
Mode	000 reaction	000 reaction	000 reaction	000 reaction	He collision	000 reaction	He collision
Product ion	TiNH3	V	CrNH <sub>3</sub>	Cr	ZnNH <sub>3</sub>	Zn	Zn
BEC, ppt	2	0.1	50	6	1.5	1	1
7700s He	60	3	8	1			

Results and Discussion

**2000ppm Si matrix**

Most manufacturers of semiconductor devices routinely analyze Si VPD samples which sometimes contain high Si matrix. Si matrix as high as 2000 ppm produces polyatomic ions of Si that interfere with P and Ti. Elimination of these interferences is shown below. A low uptake nebulizer (50 mL/min) and robust plasma conditions were applied. Si solution was made from Si wafer, but the solution may have been contaminated.

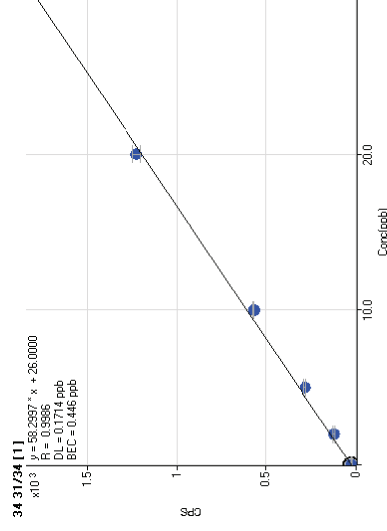


Figure 3. Calibration Curve of Phosphorus

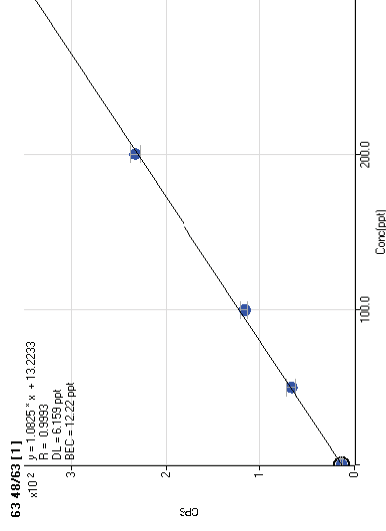


Figure 4. Calibration curve of Titanium

Conclusions

ICP-QQQ works very well to avoid spectral interferences which could not be solved by conventional collision/reaction technology. It makes it possible to determine ultra trace impurities even in complex mixtures of high purity chemicals such as HF, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>.