

## ENVIRONMENTAL ANALYSIS

# MONITORING FOR METALDEHYDE IN RAW, PROCESS AND POTABLE WATERS USING DIRECT AQUEOUS INJECTION ON THE AGILENT 6490 LC/MS/MS

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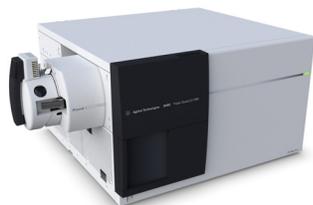
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### ABSTRACT

A method for the determination of metaldehyde in raw, process and potable waters has been developed on the Agilent 6490 LC/MS/MS using direct aqueous injection. The range of application for this method is up to 0.3 µg/L but can be extended up to 2 µg/L as necessary. Recoveries are within +/- 5% for all water types and the method achieves a limit of detection of 0.009 µg/L.



### INTRODUCTION

Metaldehyde is a molluscicide that is widely used by farmers and gardeners to control slugs and snails in a wide variety of crops. It can reach watercourses either directly during application or through run-off during periods of high or prolonged rainfall.

In Europe, the Drinking Water Directive 98/83/EC prescribes that potable tap water should contain less than 0.1 µg/L of any pesticide [1]. The main process used to remove pesticides from water is filtration through granular activated charcoal (GAC). This technology is very efficient at removing most pesticides from water. However, the characteristics of metaldehyde mean that it is not effectively removed by GAC, and its relatively simple chemical structure means that it cannot be broken down by other water treatment processes using chlorine or ozone. So, where levels exceed the drinking water standard in rivers and lakes, there is the potential risk that they may also exceed in the final drinking water, unless the water can be blended with an uncontaminated source.

This solution note outlines a robust, sensitive method that has been developed for the routine determination of metaldehyde in raw, process and potable waters, using direct aqueous injection on the Agilent 6490 LC/MS/MS.



## ANALYTICAL TECHNIQUE

### Sample Preparation

- Direct aqueous injection onto the Agilent 6490 LC/MS/MS

### INSTRUMENTATION

- Agilent 1260 HPLC System
- Agilent 6490 Triple Quadrupole System with Jet Stream Interface

### Agilent 1260 HPLC Operating Conditions

Analytical Column	Agilent Poroshell 120 EC-C18 2.1 x 75 mm, 2.7 µm
Guard Column	Agilent Poroshell 120 EC-C18 2.1 x 5 mm, 2.7 µm
Column Temperature	60°C
Injection Volume	100 µL
Mobile Phase	A = 0.1 % Acetic Acid in DI Water B = Acetonitrile
Flow Rate	0.45 mL/min
Run Time	10 minutes

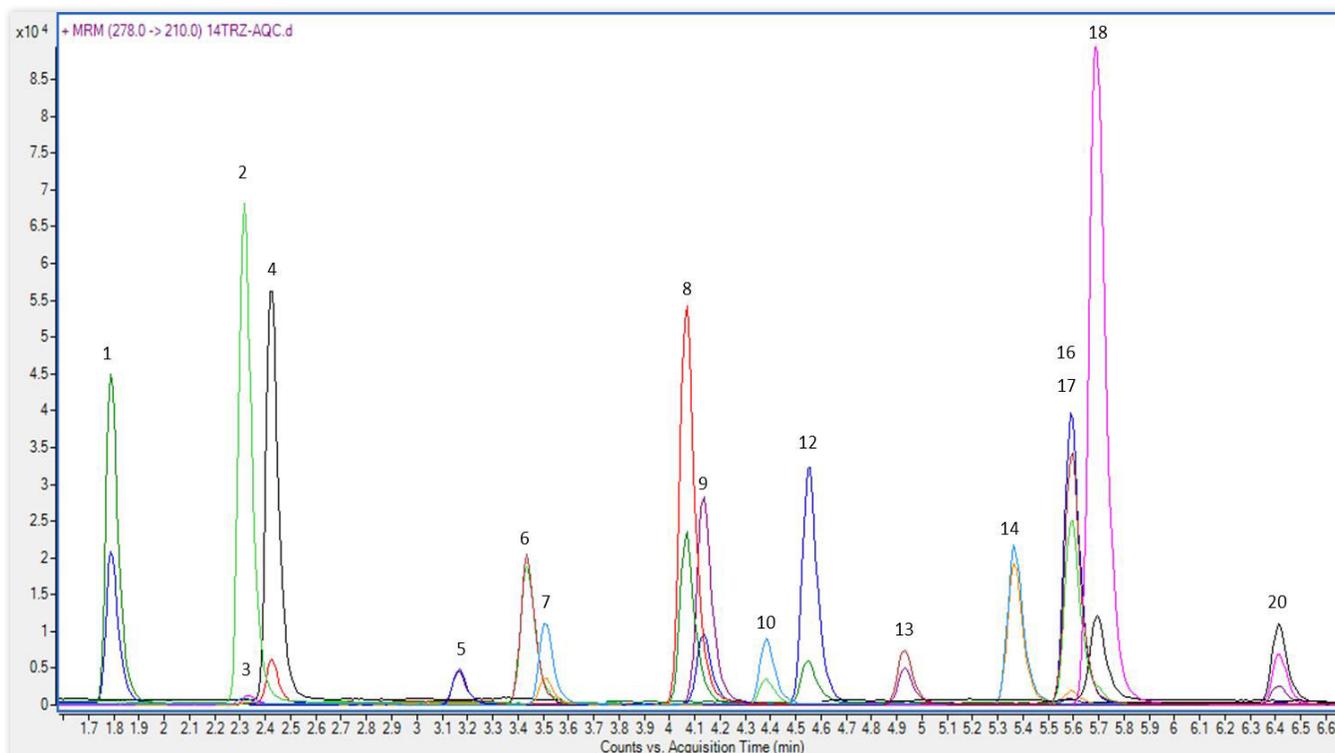
## RESULTS AND DISCUSSION

An Agilent 6490 LC/MS/MS System, with an Agilent Poroshell analytical column, was used to determine metaldehyde, as part of a routine analytical suite of 20 compounds, including triazines and urons. A method was developed that was able to rapidly determine all 20 compounds, with a run time of 10 minutes. Using positive and negative ionisation switching on the triple quadrupole, all compounds were simultaneously determined in a single run, with 17 compounds being determined in positive ionisation mode and 3 compounds in negative ionisation mode. Table 1 lists the compounds in the analytical suite, along with their retention times, ionisation mode and limits of detection. Standards and samples were introduced onto the system by direct aqueous injection, with the automatic addition of internal standard, eliminating the need for costly and time consuming sample preparation techniques. Smaller sample volumes are required to be taken and results can be obtained faster. The method should also be more reproducible as there are no extraction variables.

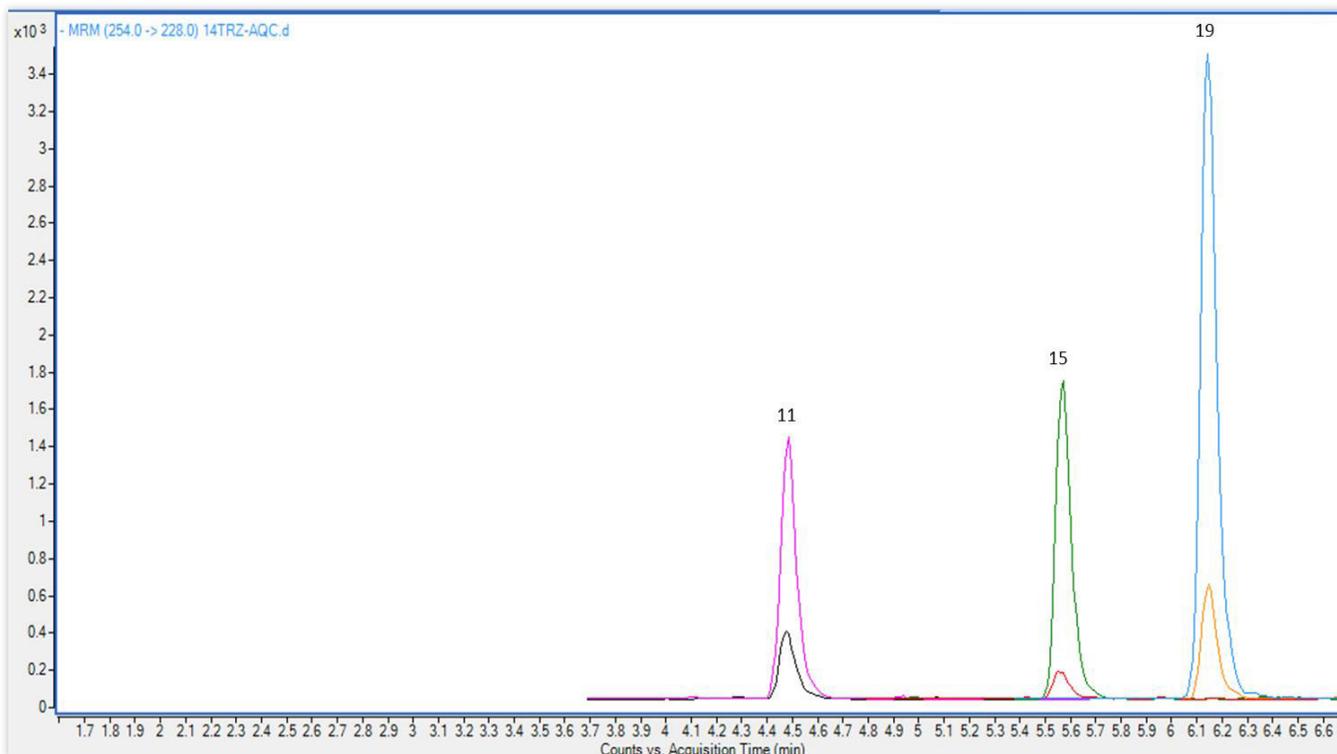
The calibration range for each compound was 0 to 0.3 µg/L, with standards at 0.05, 0.1, 0.2 and 0.3 µg/L and an analytical quality control (AQC) at 0.1 µg/L. This calibration range can be extended up to 2 µg/L with additional standards at 0.5, 1.0 and 2.0 µg/L and a high range AQC at 0.5 µg/L. Figures 1 and 2 show typical chromatograms for a 0.1 µg/L standard, for the compounds in positive and negative ionisation modes respectively. Excellent chromatography has been achieved for all compounds. Metaldehyde was determined in positive ionisation mode and comes off towards the beginning of the analytical run at 2.34 minutes.

Peak	Compound	Class	RT, min	Ionisation Mode	LOD, µg/L
1	Carbendazim	Fungicide	1.79	Positive	0.005
2	Quinmerac	Herbicide	2.32	Positive	0.005
3	Metaldehyde	Molluscicide	2.34	Positive	0.009
4	Desethyl atrazine	Triazine Metabolite	2.42	Positive	0.006
5	Carbetamide	Herbicide	3.17	Positive	0.009
6	Simazine	Triazine Herbicide	3.44	Positive	0.004
7	Cyanazine	Triazine Herbicide	3.51	Positive	0.007
8	Methabenzthiazuron	Urea Herbicide	4.07	Positive	0.005
9	Chlortoluron	Phenylurea Herbicide	4.14	Positive	0.005
10	Atrazine	Triazine Herbicide	4.38	Positive	0.004
11	Diuron	Phenylurea Herbicide	4.49	Negative	0.009
12	Isoproturon	Phenylurea Herbicide	4.56	Positive	0.004
13	Metazachlor	Herbicide	4.93	Positive	0.005
14	Propazine	Triazine Herbicide	5.36	Positive	0.004
15	Linuron	Phenylurea Herbicide	5.57	Negative	0.008
16	Terbutylazine	Triazine Herbicide	5.59	Positive	0.006
17	Prometryn	Triazine Herbicide	5.60	Positive	0.003
18	Terbutryn	Triazine Herbicide	5.69	Positive	0.005
19	Propyzamide	Herbicide	6.15	Negative	0.007
20	Trietazine	Triazine Herbicide	6.41	Positive	0.006

**Table 1.** Analytical Suite Compounds, Retention Times and Limits of Detection.

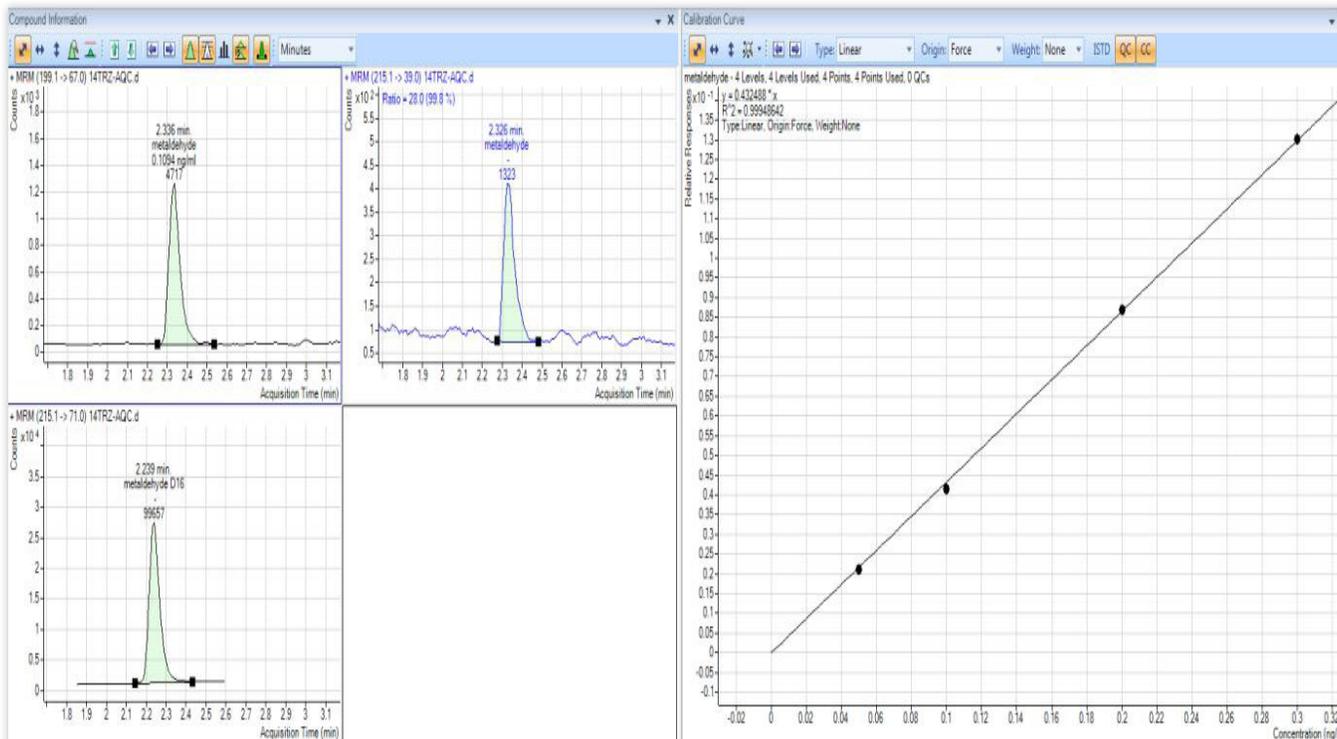


**Figure 1.** 0.1 µg/L Standard Chromatogram - Positive Ionisation Mode Compounds.



**Figure 2.** 0.1 µg/L Standard Chromatogram - Negative Ionisation Mode Compounds.

Figure 3 shows a typical metaldehyde calibration curve and compound information for a 0.1 µg/L metaldehyde standard, using metaldehyde-D16 as the internal standard.



**Figure 3.** Metaldehyde Compound Information and Calibration Curve.

A full method validation has been performed for this analytical method, based on NS30 'A Manual on Analytical Quality Control for the Water Industry' [2]. A summary of the detection limits for all the compounds are listed in Table 1. The validation procedure requires a range of water types to be tested. Three different water types were each spiked with 0.1 µg/L of standard. The spiked and unspiked samples were then analysed multiple times over a number of days in order to calculate the recoveries for the different water types. A summary of the recoveries for metaldehyde are shown in Table 2.

<b>Water Type</b>	<b>% Recovery</b>	<b>% Std Dev</b>
Clean Hard Water	97.62	4.99
Clean Soft Water	98.08	3.97
Raw Water	96.08	5.16

**Table 2.** Performance Data for Metaldehyde.

## **CONCLUSIONS**

A robust, sensitive method has been developed for the determination of metaldehyde in raw, process and potable waters using direct aqueous injection on the Agilent 6490 LC/MS/MS. Using an injection volume of 100 µL, this method demonstrates excellent linearity and sensitivity, with a calibration range up to 0.3 µg/L, which is extendable up to 2 µg/L. Recoveries are within +/- 5% for all water types and the method achieves a limit of detection of 0.009 µg/L.

## **REFERENCES**

1. Official Journal of the European Communities, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.
2. Cheeseman R.V., Wilson A.L. and Gardner M.J. (1989) 'A Manual on Analytical Quality Control for the Water Industry', WRc report NS30.



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