Chromatography Technical Note No AS123

A fully automated and quantitative method for Metaldehyde in water using GC/QqQ

Anaïs Maury, Dan Carrier & Paul Roberts, Anatune Ltd. Girton, Cambridgeshire (UK).

Introduction

Damage to crops from slugs and snails is a growing problem in the UK. Metaldehyde, a white, crystalline solid, is principally used as a contact molluscicide, commonly applied in the form of slug pellets. It is estimated that over 8 % of the area covered by arable crops is treated with Metaldehyde. Recent concerns have been raised that relatively high levels of Metaldehyde are being found in surface waters, due to its persistence in the environment and its moderate solubility in water. The UK regulatory limit for Metaldehyde in drinking water is 0.1 µg/l.
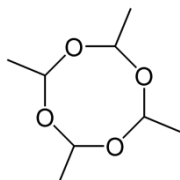
Figure 1 shows the structure of Metaldehyde.

Figure 1: Structure of Metaldehyde

Within this application note, we show how SPE can be fully automated to enrich Metaldehyde from water samples using ITSP (Instrument Top Sample Preparation) cartridges packed with 20 mg of Biotage ENV sorbent. ITSP is a consumable cartridge (manufactured by ITSP Solutions) designed to automate SPE on the Gerstel MPS (MultiPurpose Sampler).

Earlier this year, we installed an Agilent 7000 GC/MS triple Quadrupole at Anatune. By using the GC/MS Triple Quadrupole in Multiple Reaction Monitoring (MRM) mode, we were able to develop a highly selective and sensitive method for Metaldehyde.

Figure 2 shows a photograph of the instrumentation which was used for this study.

Figure 2: Gerstel Dual Head MPS with GC/MS/MS Triple Quadrupole

Figure 3 shows a more detailed photograph of the dual head MPS. The left head is configured with a 10 µl GC syringe. The right head is configured with a 2.5 ml headspace syringe.

Figure 3: Detail photograph for automated SPE

Instrumentation

Gerstel Multipurpose Sampler (MPS) 2 XL Dual head
Gerstel Cooled Injection System (CIS) 4
Instrument Top Sample Preparation (ITSP), ITSP Solutions
Maestro (version 1.4.18.25/3.5)
Agilent 7000 GC-Triple Quadrupole
Agilent GC 7890A

Method

GC/MS conditions:

Large volume injection 10 µl (injection speed 1.44 µl/s)

Injection mode:	PTV solvent vent
CIS 4:	Tenax liner
CIS 4 Temp Program:	10 °C (2 minutes); 12 °C/s to 250 °C (10 minutes)
Column:	DB-5MS 30 m x 0.25 mm x 0.25 µm
Thermal gradient:	50°C (5 minutes); 50°C/min to 300°C (hold 2 minutes)

MS: EI, MRM performed using two transitions for each analytes (Table 1).

	Precursor ion (m/z)	Product ion (m/z)
Metaldehyde	89.0	45.1
	89.0	43.1
Metaldehyde d-16	98.1	50.1
	98.1	46.1

Table 1: MRM transitions used

Extraction procedure:

Using the right MPS fitted with a 2.5 ml headspace syringe (SPE needle), the ITSP cartridge (Biotage ENV) was conditioned with 2 ml dichloromethane (DCM), 2 ml of methanol followed by 2.5 ml of HPLC grade water to equilibrate the cartridge. 10 ml of sample (in water) was then loaded and the cartridge was dried for 15 minutes with nitrogen using the headspace syringe. Drying is a critical step to get the best recovery of Metaldehyde and Metaldehyde-d16 from the cartridge. After drying, 400 µl of dichloromethane was used to elute the Metaldehyde and Metaldehyde-d16 into a standard 2 ml GC vial.

Assuming 100 % recovery of Metaldehyde from the cartridge, eluting in 400 µl of DCM will give a 25 fold increase in Metaldehyde concentration.

The left MPS head fitted with a 10 µl syringe was used to inject 10 µl of the extract into the Cooled Injection System (CIS 4).

A seven point calibration for Metaldehyde was prepared in water at concentrations ranging from 0.04 µg/l to 0.8 µg/l keeping the Metaldehyde-d16 consistent at 0.32 µg/l.

Results

Figure 4 shows a comparison of calibration level 1 (Metaldehyde at 0.04 µg/l) and a blank.
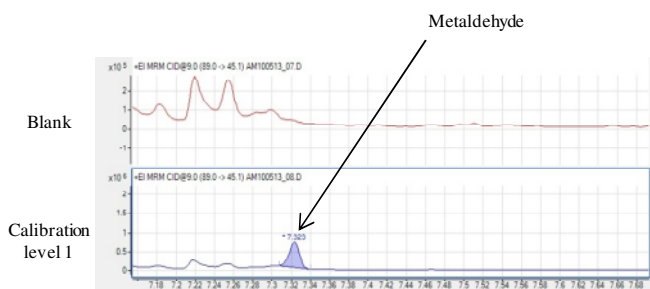

Figure 4: MRM (transition 89 to 45 m/z) chromatogram of a Blank and the Calibration level 1 (Metaldehyde 0.04 µg/l)

Figure 5 shows a calibration plot for Metaldehyde from extracted water samples. A correlation coefficient of 0.999 was achieved. The theoretical detection limit for Metaldehyde was calculated to be 0.002 µg/l based upon the S/N ratio for the bottom calibration point.
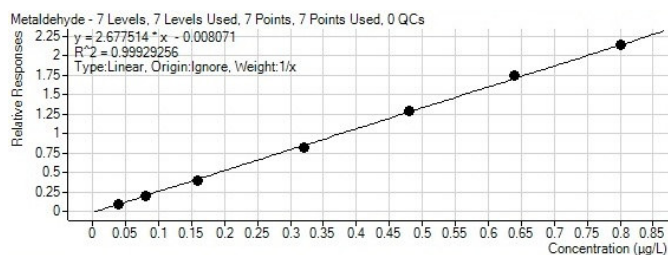

Figure 5: Linearity plot of Metaldehyde from extracted water samples

Recovery experiments have been carried out at two different concentrations: 0.06 µg/l and 0.7 µg/l. Table 2 shows this recovery data from replicate SPE extractions, using an internal standard.

Amount spiked (µg/l)	0.0608	0.7040
Amount detected (µg/l)	0.0573	0.6385
	0.0572	0.7190
	0.0600	0.7044
	0.0562	0.7225
	0.0564	0.7220
Mean	0.0574	0.7013
SD	0.0015	0.0358
% RSD	2.61	5.11
% Recovery	94.49	99.62

Table 2: Recovery data for Metaldehyde from extracted water samples using ITSP

Discussion

This application note shows how the extraction of Metaldehyde from water samples can be fully automated using ITSP.
Further work is due to be completed on "real" surface and groundwater samples from a variety of sources, to establish method robustness and variability. Additionally recovery and precision in these "real" samples will be determined via the standard addition technique.