*Chromatography Technical Note No AS166*

# On-line Monitor for Metaldehyde in Surface and Ground Water

*Richard Davis, Jeff Stubbs. Anatune Ltd. Girton, Cambridgeshire (UK)*
*Debbie Loftus-Holden, David Walker, Matt Rawlinson. Affinity Water Ltd.*

## *Introduction*

Metaldehyde is primarily used as a contact molluscicide in the control of slugs and snails in the UK. The use of metaldehyde is common in the agricultural industry surface waters and karstic groundwater abstractions can be impacted by metaldehyde, due to its persistence in the environment its moderate solubility in water and the difficulty in treating this with conventional pesticide processes (Granular activated carbon and ozone). The UK regulatory limit for metaldehyde in drinking water is 0.1µg/L.

The concentration of metaldehyde in surface and ground waters increases after rainfall due to surface water run-off from agricultural land. There is therefore a need for a real-time online monitor on treatment works capable of detecting metaldehyde below the regulatory limit of 0.1µg/L. With this challenge Anatune has worked closely with Affinity Water, the UK's largest water only company, to provide this solution.

A previous application note (AS123) demonstrated how extraction of metaldehyde from water could be automated using instrument top sample preparation (ITSP), a miniaturised form of solid phase extraction (SPE). This application used an Agilent 7000 GC/MS a Triple Quadrupole GCMS with automated sample preparation. This system was demonstrated to detect metaldehyde below the 0.1µg/L limit.

Requests to automate sample preparation for the analysis of metaldehyde were made to Anatune by laboratories from the Water Industry. Interest for this was due to the increasing number of samples and length of time to carry out these steps manually in the laboratory. Automation of the sample preparation has been shown reduce analyst processing time and gain better quality data. It was decided for this project to take this as the starting point for the analytical work and incorporate this into a Water Treatment Works environment.

It can currently take up to 10 working days to obtain metaldehyde test results due to the sheer volume of samples Affinity Water analyses for. This coupled with the design of a new metaldehyde treatment process were the key drivers for the Affinity Water Pesticide Programme team to explore a new approach to detecting metaldehyde in waters. In 2015, Affinity Water and Anatune Ltd started discussions about the application of this instrument to take quasi real-time samples of the raw and partially treated water on a Water Treatment Works (WTW).

In September 2016, an 'online metaldehyde monitor' trial commenced at a 36 Ml/d Affinity Water karstic groundwater treatment works with four sources in Hertfordshire analysing metaldehyde concentrations from three inlets at different stages of treatment.

Whilst this piece of equipment has been used for many years in a controlled laboratory setting, this is the first installation on a WTW in the UK and an innovative approach for online metaldehyde monitoring.

This work has a combined peak flow of 36Ml/d and average flow of 31.5Ml/d, fed by four sources, all of which experience varying levels of metaldehyde and turbidity. This works has several automated online process controls in place for nitrates, turbidity, UV absorbance to ensure compliance with acceptable levels in the raw and partially treated water.

The aim of the trial for Affinity Water was to determine whether this type of automated system could provide robust and reliable metaldehyde results in real time under the varying water quality conditions in an operational environment. Faster reaction to changes in metaldehyde levels would facilitate a better management of abstraction and reduce the risk of exceedances.

**Figure 1. Installation at Affinity Water's treatment works.**

The instrumentation required specific conditions in which to be housed to maintain correct operating conditions. Working with water industry MEICA partner, JR Pridham Services Ltd (JRP) they delivered one-stop enabling works and installation solutions. This can be seen in figure 1. JRP through collaboration with Anatune worked together to build a purpose-built laboratory-grade environment that the instrument would be installed in. This encompassed lab benching, wash area, extraction, ventilation and temperature control.

**Figure 2. Agilent 7000 GC/MS/MS and Dual Head GERSTEL MPS with on-line ITSP, SFS and flow cell at Affinity Water's treatment works.**

**Anatune Ltd**, Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223279210 Fax: +44 (0) 1223279253 Email: info@anatune.co.uk Internet: www.anatune.co.uk

Figure 2 shows the installation at the Affinity Water Treatment works. This installation replicates a laboratory system used for routine Metaldehyde analysis of water samples with the exception of 1 item. A flow cell is needed for the instrument to take samples in an online fashion from.

Another previous application note (AS134) describes the use of a flow cell as a technique to enable on-line real-time sampling of liquids. Figure 3 shows the flow cell in more detail.

**Figure 3. Close up of Flow Cell**

Following several months of trial evidence and data Affinity Water will determine if this can be built into their overall solution to managing metaldehyde for this site. Trial evidence to date is promising.

## *Instrumentation*

Dual Head GERSTEL MPS 2 XT
GERSTEL Cooled Injection System (*CIS) 4*
Maestro software integrated
Agilent 7000 GC-Triple Quadrupole
Agilent GC 7890A
Instrument Top Sample Preparation (ITSP), ITSP Solutions
GERSTEL Solvent Filling Station (SFS)
Flow Cell

## *Method*

Agilent GC/MS/MS conditions:

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

Injection mode: PTV solvent vent
CIS 4: glass wool 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 analyte (Table 1).

| | Precursor ion (m/z) | Product ion (m/z) |
|---|---|---|
| Metaldehyde | 89.0 | 45.1 |
| | 89.0 | 29.1 |
| Metaldehyde-d16 | 98.1 | 50.1 |
| | 98.1 | 46.1 |

**Table 1: MRM transitions used**

**Extraction procedure:**

Using the left MPS head 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 ml of HPLC grade water to equilibrate the cartridge. 7.5 ml of sample (in water) and 1mL of internal standard 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.

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

**On-line set up:**

A bespoke cabin was modified to replicate a remote laboratory environment, housing the instrument, supporting consumables and ancillaries, IT, sampling preparation and an office.

There were a number of modifications required in order to enable the online monitoring of metaldehyde for this trial. More advanced software and a Programmable Logic Controller (PLC) were installed to allow the instrument to read to the telemetry systems.

There are three inlets at different stages of treatment which were required to be monitored. These are:

- Inlet 1: blend of three raw groundwater sources;
- Inlet 2: post-clarification on the fourth groundwater source
- Inlet 3: post-GAC on all four sources combined.

The software allows the instrument to select each of the different inlets for analysis, in sequential order through each separate and relevant sample line. Selection was carried out via the software requesting to open a relevant solenoid. While a sample line is open and undergoing readiness to be sampled by the instrument, the other 2 sample lines run to waste.

To ensure reproducible sampling, flow cells were calibrated to supply water at > 1.0 L/min. Following the opening of the selected solenoid valve, and a flow rate within required sampling parameters, the sample would flow up to the online flow cell which was mounted on the GERSTEL MPS Rail (Figure 3).

If the required flow was not reached, then sampling was automatically switched to the next sample line using intelligent software.
Figure 4 shows the on-line mechanism to control flow.

A turbidity of less than 1 NTU was required to carry out the automated solid phase extraction. The approach from Affinity Water, via JRP Ltd. was to install a 3-level tapered filtration system (Figure 5) to ensure that a turbidity of less than 1 NTU was consistently arriving at the instrument. This would in turn ensure that the ITSP solid phase extraction cartridge would not be blocked by incoming turbidity and was critical for reliable operation with the minimum amount of downtime

**Validation parameters:**

Validation included testing linearity, accuracy, precision, instrument precision, intermediate precision, limit of detection (LOD), and limit of quantitation (LOQ). In addition, six replicates of two proficiency test (PT) samples from LGC Aquacheck PT scheme were analysed. Table 2 summarises the validation criteria.

**Anatune Ltd**, Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA, UK
Tel: +44 (0) 1223279210 Fax: +44 (0) 1223279253 Email: info@anatune.co.uk Internet: www.anatune.co.uk

To ensure a robust, accurate and reliable system was provided to Affinity Water, these agreed performance criteria were determined that the system had to meet.

Below shows the criteria, along with the actual data from the system. All criteria asked for were met comfortably by the instrument performance.

**Figure 4. On-line flow monitors**

**Figure 5. On-line inlet Agilent 7000 GC-Triple Quadrupole filtration**

| | Criteria |
|---|---|
| Linearity | >0.990 ($r^2$) |
| 0.1µg/L Within Batch Accuracy | <20% |
| 0.1µg/L Within Batch Precision | <20% |
| 0.1µg/L Between Batch Accuracy | <20% |
| 0.1µg/L Between Batch Precision | <20% |
| 0.8µg/L Within Batch Accuracy | <20% |
| 3.2µg/L Within Batch Accuracy | <20% |
| LOD | < 0.05 µg/L |
| LOQ Within Batch Accuracy | <20% |
| LOQ Within Batch Precision | <20% |
| LOQ Between Batch Accuracy | <20% |
| LOQ Between Batch Precision | <20% |
| Instrument Precision | <20% |
| Intermediate Precision | <20% |
| AquaCheck Round 512 (z-score) | <2.0 |
| AquaCheck Round 508 (z-score) | <2.0 |

**Table 2. Validation criteria**

## *Results*

To ensure a robust, accurate and reliable system was provided to Affinity Water, agreed performance criteria were determined that the system had to meet. All validation solutions were prepared in 20mL vials and taken through the ITSP process.

**Linearity:**

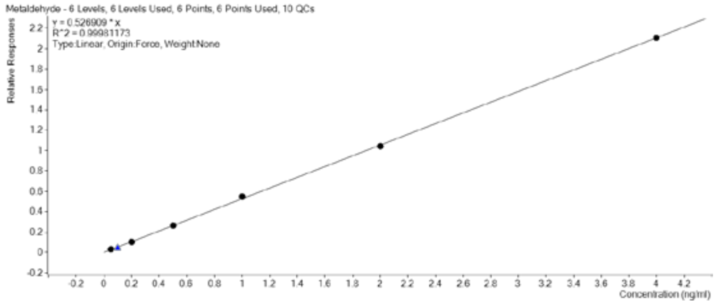


**Figure 5. Linearity**

Validation Results (Precision, Accuracy, LOD and LOQ):

| Validation Summary | Criteria | n= | Result |
|---|---|---|---|
| Linearity | >0.990 (r2) | 6 | 0.998 (r2) |
| 0.1µg/L Within Batch Accuracy | <20% | 10 | 3.0% |
| 0.1µg/L Within Batch Precision | <20% | 10 | 1.7% |
| 0.1µg/L Between Batch Accuracy | <20% | 29 | 5.1% |
| 0.1µg/L Between Batch Precision | <20% | 29 | 3.6% |
| 0.8µg/L Within Batch Accuracy | <20% | 6 | 8.1% |
| 3.2µg/L Within Batch Accuracy | <20% | 6 | 10.5% |
| LOD | < 0.05 µg/L | 10 | 0.003µg/L |
| LOQ Within Batch Accuracy | <20% | 10 | 4.6% |
| LOQ Within Batch Precision | <20% | 10 | 1.8% |
| LOQ Between Batch Accuracy | <20% | 17 | 6.3% |
| LOQ Between Batch Precision | <20% | 17 | 2.9% |
| Instrument Precision | <20% | 9 | 3.7% |
| Intermediate Precision | <20% | 9 | 4.2% |
| Aqua-Check Round 512 (z-score) | <2.0 | 6 | 0.00 |
| Aqua-Check Round 508 (z-score) | <2.0 | 6 | 0.01 |

**Table 3. Details the results from the initial validation of the on-line metaldehyde monitoring system.**

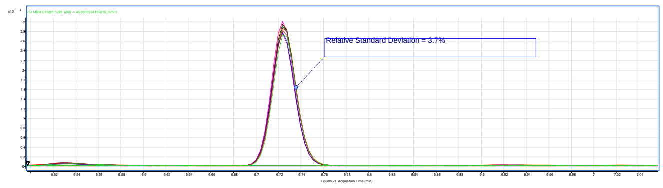


**Figure 6. Instrument Precision**

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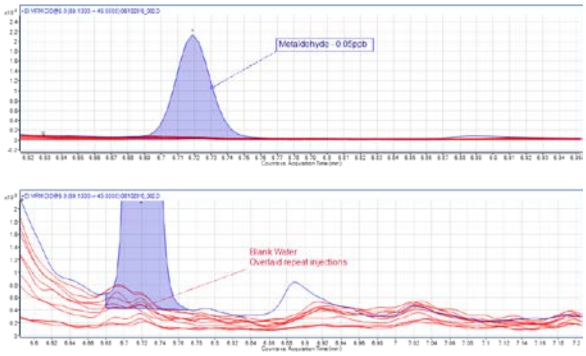


**Figure 7&8. Overlaid chromatographs of 0.05 ppb (µg/L) standard and blanks**

## *Summary*

Both repeatable and reproducible validation results were obtained for the on-line analysis of metaldehyde using ITSP cartridges on an Agilent 7000 GC/MS triple quadrupole instrument.

Sample Preparation is the key to any good analytical method and the GERSTEL MPS system delivers this key principal. It reduces the uncertainty in the analytical measurement. In this case, for an on-line monitoring solution, an additional key is ensuring the water being accepted by the instrument is of sufficient quality to maintain robust and reliable results.

Figure 5 illustrates the linearity that can be obtained using the GERSTEL MPS system, r2 0.999 and figure 6 demonstrates its precision. Table 3 displays a detailed overview of the precision and accuracy that this system delivers for both within and between batch analyses. The LGC Aqua-check result provides the on-going certainty that the method is in control. Figures 7 & 8 shows the typical noise level at the retention time relative to the blank, LOD and LOQ.

Further investigation is underway at Affinity Water to understand the impacts the varying water quality conditions may have on the instrumentation and results.

Please contact Anatune if you need any further information on this technique.

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