*Chromatography Short Note No AS92S*

# Investigations into the automated Online Solid Phase Extraction and GC-MS Analysis of Metaldehyde from Water Samples.

## Introduction

This application note describes preliminary work for an online, automated method for the extraction of metaldehyde from water samples, utilizing the Gerstel Solid Phase Extraction (SPE) station, based upon an Agilent 7890/5975C series gas chromatograph/MSD combined with a GERSTEL MPS 2 autosampler.

Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetraoxocanemetacetaldehyde) (See Figure 1) is an oligomer of acetaldehyde, which is mainly used as a contact molluscicide in the form of commercially available slug pellets.

Of the area covered by arable crops including wheat, potatoes and oil seed rape, 8% is treated with metaldehyde. Due to its persistence in the environment and its moderate solubility in water, concerns have been raised, that existing water treatment practices may not be effective in removing the compound below the regulatory limits set out by the Drinking Water Inspectorate (DWI) of 0.1 µg/L.
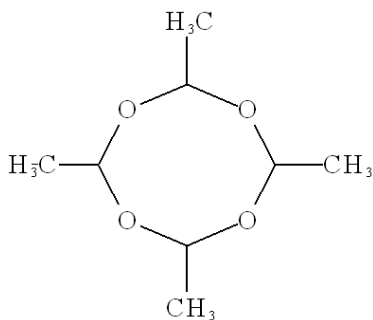


Figure 1. – Structure of metaldehyde.

## Instrumentation

- Agilent 7890A Gas Chromatograph
- 5975C Mass Selective Detector
- Agilent ChemStation
- GERSTEL MPS 2 prepstation, one beam configured for SPE, the second beam configured for liquid injection
- Anatune XLR8R.
- Anatune CoolR+

## Methodology

Metaldehyde was extracted from 40 ml water samples using Gerstel format Superclean 15 mg ENV 3ml SPE cartridges (Varian, UK). For each extraction a SPE cartridge was first cleaned with 2 ml of dichloromethane, then solvated with 2ml of methanol. The cartridge was then equilibrated with 4 ml of water in preparation for sample loading. All SPE cleaning and conditioning steps were carried out automatically using the MPS 2 at 100 µl/S.

10 ml of sample was then loaded onto the cartridge. Following sample enrichment the SPE cartridge was dried with an air push of 5 ml.
Metaldehyde was eluted from the SPE cartridge using two 200 µl aliquots into a standard 2 ml GC vial with an air push after each to remove residual solvent from interstitial sorbent spaces.

Analysis was achieved using the following conditions, 2 µl pulsed splitless injection, with an injector temperature of 280 °C. Initial oven conditions, 50 °C held for 5 minutes then ramped at 50 °C per minute to 300 °C whereby temperature was maintained for 2 minutes giving a total run time of 12 minutes. Helium was employed as the carrier gas. Separation was achieved using a HP5-MS 30m x 0.25 mm ID x 0.5 µm film thickness column, with the transfer line being held at 320 °C

The mass spectrometer was operated in single ion monitoring mode using the following conditions, source 300 °C and quad 180 °C Metaldehyde was quantified using a target ion of 45.0, and a qualifier ion of 89.0. Under the following conditions metaldehyde displayed an approximate retention time of 7.76 minutes.

The system is operated via the Gerstel Maestro software package which is fully integrated into MSD Chemstation, and gives users full online prep ahead functionality. This means that sample preparation steps such as SPE occur during the preceding samples' analysis. The integrated nature of the software package means that transcription errors can be eliminated and features a single point of control.

None of the stages were fully optimised, but the study was conducted to offer an insight as to the suitability of automated online SPE in the extraction and analysis of metaldehyde from water samples.

## Results

Linearity of the system was first investigated using solvent calibration standards, the system exhibited a linear calibration between 10 and 1000 ng/L with a correlation coefficient of 0.998.
Linearity of the system was also investigated in spiked water samples between 10 and 1000 ng/L whereby a linear correlation coefficient was also observed of 0.996. (See Figure 2).
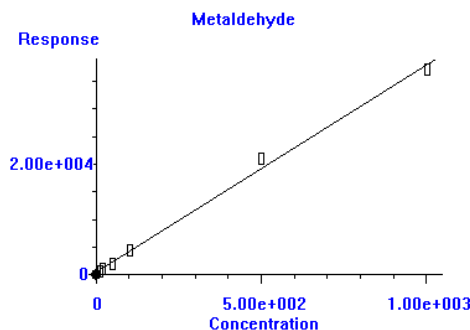


Figure 2. – Metaldehyde calibration curve in spiked water samples.

Further data was collected from spiking samples at 100 ng/L (n=5) with an appropriate amount of standard and then extracting them and analysing against the solvent calibration. Results from this analysis provided preliminary absolute recovery data of ~ 63% with a standard deviation of 5.58 and a % RSD of 8.9.
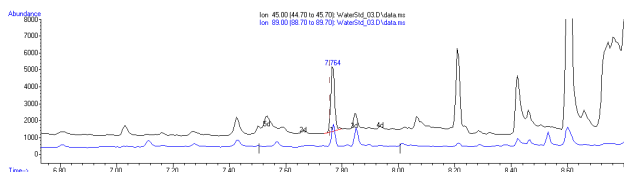


Figure 3. - Typical extracted ion chromatogram of a 100 ng/L standard.

## *Conclusions*

Initial data appears to be promising as further optimisations potentially could be made to the SPE protocol to enhance recovery of metaldehye. Additionally the use of a suitable internal standard in the procedure, added to correct for losses occurring during sample preparation could be incorporated.

The system could be employed to determine metaldehyde in bottled samples as was used in these investigations, but additionally by fitting a flow cell onto the MPS 2 online stream sampling may be made in an unattended fashion.