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AS168

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INITIAL WORK FOR AUTOMATION OF A BSTFA DERIVATISATION FOR PHENOLIC COMPOUNDS IN WATER

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INTRODUCTION

Phenolic compounds are a group of chemicals which are detectable to the human palate as metallic tastes at low concentrations in drinking water. The reaction of hypochlorite and phenolic acids produces chlorinated phenols a by-product as to does degradation of phenoxy herbicides. 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol are most likely of the chlorinated phenolic compounds to occur in drinking water as they are by-products of the disinfection process.

Due to their polarity the phenolic compounds do not chromatograph well on commonly used non-polar column phases such as DB-5MS. Peak tailing is often a consequence of this and can affect quantitative reproducibility. Derivatives of phenols produces more volatile and less polar compounds whose chromatographic behaviour is more suited to non-polar column phases.

The phenolic and chlorinated phenolic compounds are weak to moderately acidic and pKa values of the compounds in this study were in the range of 5-10 and completely unionised in highly acidic conditions. As it is routine in water testing to collect samples preserved with acid less sample preparation is required to facilitate the liquid-liquid extraction (LLE).

The aim of this study was to demonstrate an automated technique as an alternative to the previous described automation in application note AS167. This work was a follow on from the previous application using the Agilent 5977B single quadrupole mass spectrometer with High Efficiency Source (HES).

This application note describes the method development of an on-line automated solution for phenolic and chlorinated phenolic compounds with derivatisation by N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA). Development was in conjunction with Paul Leather, Environment Agency in July-Aug 2016. This method uses and automated liquid-liquid extraction with vigorous agitation using the mVorx and derivatisation by agitation and heating on the GERSTEL Agitator.

INSTRUMENTATION

Dual Head GERSTEL MPS XT
GERSTEL mVorx
GERSTEL Agitator
Maestro software integrated
Agilent 7890 GC with a 5977B mass spectrometer with High Efficiency Source (HES)

Figure 1: GERSTEL Dual Head with Agilent 5977B HES

METHOD

Samples of cage material were packed into empty GERSTEL thermal desorption tubes and plugged with a small amount of quartz wool. This was attached to the inlet of the SIFT-MS using a short piece of silicone tubing. A 1 L Tedlar bag containing the required gas mix was attached to the other end of the tube, again using silicone tubing and the tap opened. Figure 3 shows the tube and Tedlar bag used. The uptake of formaldehyde into the cage material was then monitored using the SIFT-MS sampling continuously at 20 mL/min.

A suite of twenty six phenolic compounds were prepared firstly at a concentration of 2 ug/mL and analysed in full scan mode after derivatisation with BSTFA to determine the most abundant ions. The chromatography was optimised and a method in Selected Ion Monitoring (SIM) mode was then applied to analyse the extracts from the automated sample preparation. This work was on a 30 M 0.25 mm I.D DB-5MS UI column.

Solutions were prepared at concentrations of 50, 100, 500, 1000 and 2000 ng/L in purified water by automated addition of concentrated stock standards by the MPS.

The aqueous standards were firstly acidified by addition of sulfuric acid to 8 mL of water to replicate the acid added as preservative in the sample collection. An aliquot of isohexane was added to the sample followed by vigorous mixing using the mVorx. A small volume of a polar solvent was added to break up emulsions before transferring a portion of the solvent layer to a GC vial. Derivatisation by addition of excess BSTFA was performed firstly at room temperature and also at 90° C for 50 mins.

1 µL was then subsequently injected directly into the MMI inlet of the Agilent 6890 GC with 5977B mass spectrometer. Overall run time was optimised by use of the CoolR+ to facilitate rapid cooling and equilibration of the GC oven.

RESULTS

The full scan after derivatisation at room temperature for a 2 µg/mL standard is shown in figure 2. Optimisation was not completed for the derivatisation as it was not required as sensitivity was adequate without optimisation.

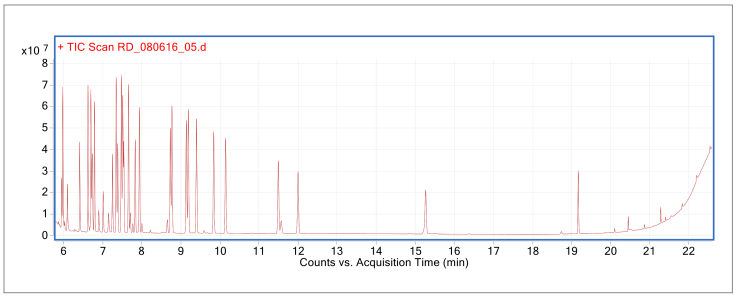

Figure 2: Full scan BSTFA derivatisation of a 2 µg/mL phenol standard.

The original GC conditions were as per the method in AS161. Resolution of the target compounds after BSTFA derivatisation was sufficient that the oven temperature gradient was increased after 10 minutes to elute the remaining compounds and decrease the run time to 13 minutes, see figure 3.

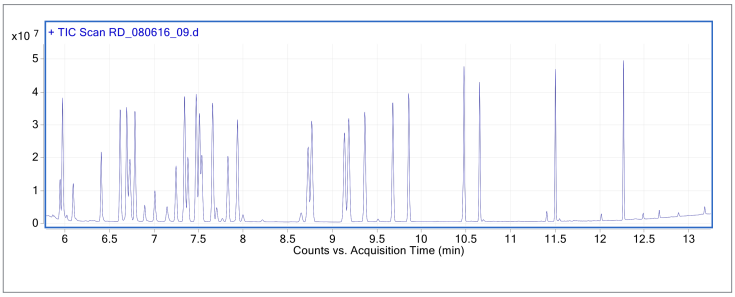

Figure 2: Full scan BSTFA derivatisation of a 2µg/mL phenol standard after optimisation of GC run time.

The original GC conditions were as per the method in AS161. Resolution of the target compounds after BSTFA derivatisation was sufficient that the oven temperature gradient was increased after 10 minutes to elute the remaining compounds and decrease the run time to 13 minutes, see figure 3.

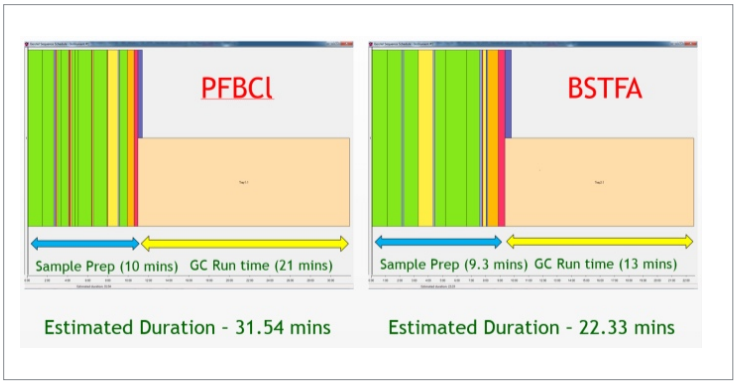

Figure 4: Maestro Preparation Sequences for PFBCl and BSTFA automation

The use of BSTFA as a derivatising agent for phenols analysed with an EI source yields mass spectra with characteristic fragmentation patterns. A good response in EI for the molecular ion [M](+) and common losses are shown in figure 5.

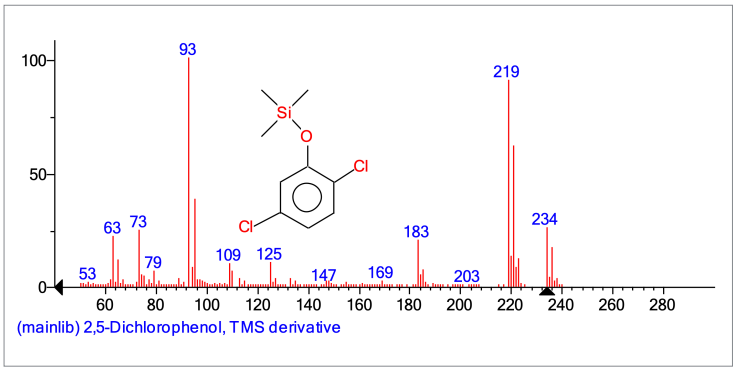

Figure 5: 2,3-dichlorophenol-TMS NIST 2014

The quantifier and qualifier ions selected for the final method are given in table 1.

Table 1: SIM ions for EI method

TMS Derivative	SIM Ions
Phenol	155,161
2-methyl phenol	165,180
3-methyl phenol	165,180
4-methyl phenol	165,180
2-Ethyl Phenol	179,194
2,6-dimethyl phenol	179,194
3-chlorophenol	185,200
4-chlorophenol	185,200
2,5-dimethyl phenol	179,194
2-Chlorophenol	185,200
2,4-dimethylphenol	179,194
2,3-dimethyl Phenol	179,164
3,5-dimethylphenol	179,164
2,3-dimethyl phenol	179,164
4-Chloro-2-methylphenol	199,214
3,4-dimethylphenol	179,164
4-Chloro-3-methylphenol	199,214
2,5-dichlorophenol	219,183,234
2,4-dichlorophenol	219,183,234
2,6-dichlorophenol	219,183,234
2,3-dichlorophenol	219,183,234
4-chloro-3,5-dimethylphenol	229,213
2,4,6-trichlorophenol	268,270
2,4,5-trichlorophenol	268,270
2,3,5,6-tetrachlorophenol	289,304
Pentachlorophenol	323,328

Linearity and precision were not carried out for the 26 phenolic and chlorinated phenolic compounds, as this was initial proof of concept work. A standard was extracted from purified water at 50 ng/L and ran in SIM mode and all target compounds could be determined figure 6 shows the extracted SIM ions.

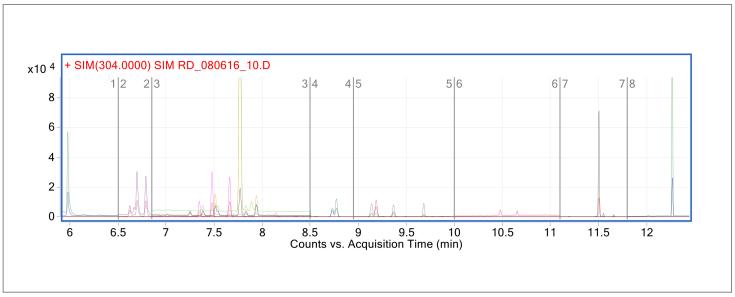

Figure 6: SIM ions 50 ng/L extract

DEMONSTRATION

This initial investigation demonstrates how the improved sensitivity of the 5977B can offer the option of different approach to LLE for phenols in water.

Further investigation is required to optimize the derivatisation yield, but it was sufficient to demonstrate sensitivity at the lowest calibration level for all 26 phenols. If required a larger injection volume, optimization of the LLE or instrument settings could be utilised to achieve lower limits of detection.

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