Chromatography Technical Note No AS134

The on-line measurement of VOCs in Flowing water

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Introduction

The measurement of chemicals in óon-lineô situations can be critical in waste monitoring and process control. A special flow cell enables on-line sampling of liquid process streams. Samples can be taken automatically from the flow cell as defined in the GC method at user defined intervals. Samples are injected into the GC for immediate analysis or can be stored in a vial for later use. In combination with a Gerstel multipurpose sampler (MPS), sampling directly from a water stream and subsequent analysis of sample headspace, can be fully automated.

The detection of volatile or semi-volatile compounds in waste water can be critical in demonstrating compliance. Online monitoring of volatile organic compounds enables rapid decisions to be made.

Within this application note, we show how the flow cell can be used to fully automate sampling from an effluent stream with immediate analysis for residual solvents using static headspace GC-FID. The method can be adapted to sample from smaller (2ml) vials in order to maintain a high frequency of sampling with minimum operator input.

Figure 1: Gerstel Dual Head MPS with flow cell and GC FID

One head is configured with a liquid syringe to enable sampling from the flow cell and addition of internal standard. The second head has a heated headspace syringe for headspace sampling and injection. Figure 2 shows a more detailed photograph of the Flow cell unit.

Figure 2: Detail photograph of Flow cell

The flow-cell consists of a stainless-steel chamber fitted with inlet and outlet ports and a septum port that can be accessed with a syringe. In this application a 1ml sample aliquot was taken for subsequent headspace analysis.

Instrumentation

Agilent GC 7890A with FID detector
Dual head Gerstel MPS 2 Left hand headspace (2.5ml or 1ml) syringe, right hand 1ml liquid syringe.
Agilent MSD Chemstation software (version E.02.02.1431)
Maestro software integrated (version 1.4.18.25/3.5)

Method

Headspace parameters:

Incubation at 90°C for 5 minutes
2ml Vials : 0.75ml sample, sample 300ul of headspace
10ml Vials: 1ml sample, sample 1ml headspace

GC-FID parameters:

Split injection (50:1) at 250°C
Column: DB-624
FID: Temperature 300 °C,

Flow cell sampling procedure:

At pre-determined intervals, an aliquot of water is taken from the flow-cell and dispensed into a vial. Next, the same syringe adds internal standard to the sample vial.
The sample vial is transported to the agitator where it is heated and mixed so that the volatile compounds from the water sample equilibrate into the headspace in the vial.
Once equilibrium has been achieved (or after a defined period of time), the injection syringe removes a defined volume of headspace and injects this into the GC.
The sequence is repeated continuously and using the maestro prep-ahead, the next sample can be ready to inject as soon as the GC program for the previous sample is complete. In this example, a sample could be taken every 15-20 minutes from the flow cell.

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Results

Using an internal standard, good reproducibility was achieved for a range of solvents in effluent. Figure 1 shows example chromatograms for a calibration standard and effluent sample. Reproducibility data (n=6) for calibration solution in water are given in Table 1.

Figure 1: Example chromatograms for solvents
(Standard concentrations range from 2 to 200ppm – see Table 1)

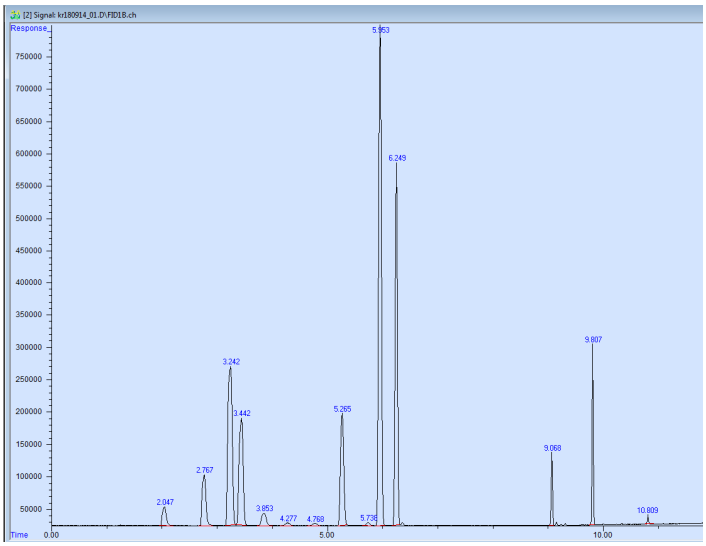

Table 1: Reproducibility for selected solvents in water (n=6) 2ml vials, 90°C for 5 minutes. (0.75ml sample, 300ul headspace)

Solvent	Retention time (mins)	Concentration (ppm)	RSD (%)
Methanol	2.1	200	2.8
Ethanol	2.8	200	3
Acetone	3.2	200	3.6
Propan-2-ol	3.4	200	1.6
MEK	5.9	200	4.6
Butan-2ol	6.3	200	2.1
Toluene	9.1	2	11.9
Mesityl Oxide	9.9	20	4.8

Discussion

This application note shows how a Multipurpose sampler (MPS) and flow cell can be used for rapid online analysis of liquid process streams.

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