Multiple headspace extraction (MHE) with syringe sampling

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Introduction

The MHE technique is demonstrated with the CombiPAL, a syringe based autosampler. The quality of the data compare well with those obtained from a loop-based sampling system.

MHE is generally regarded as the method of choice with analysis of difficult headspace samples.

Matrix effects are practically eliminated with MHE and the difficulties of quantitative headspace analysis can be overcome.

Fig. 1. Headspace sampling involves easy sample handling and preparation!

MHE Tool for the CombiPAL

Multiple headspace extraction involves a sequence of pressurizing, sampling, and venting from the sample for each of the extraction steps. Traditionally, the pressurizing and venting steps are difficult to control with a syringe-based system.

A simple tool was manufactured, allowing for the controlled venting of the pressurized sample vial after each sample extraction step. The operation of the tool is fully integrated into the CycleComposer software used to control the CombiPAL sampler.

The pressurization is done using the built-in standard functions of the CombiPAL.

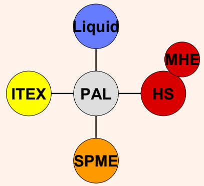
Fig. 2. The sample is withdrawn from the vial.

Fig. 3. The venting tool is positioned above the sample vial.

Fig. 4. Activating the venting tool vents the vial content to the ambient.

Versatility of the CombiPAL

The versatility of the CombiPAL as a syringe based autosampler has been enhanced by developing the MHE Tool. Syringe-based samplers are generally flexible and can accommodate various injection techniques:



Results by syringe sampling

10µg of acetone and of 2-propanol was spiked onto 50mg 5-amino salicylic acid granulate sample in a 10ml headspace vial.

Fig. 5. shows the decay of the GC-signal for acetone and 2-propanol. Theoretically, one expects an exponential decay, this is confirmed by the semilogarithmic plots of Fig. 6.

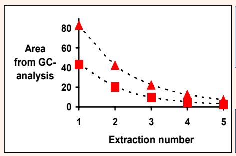


Fig. 5. Signal as a function of the number of extractions.

■ acetone
▲ 2-propanol

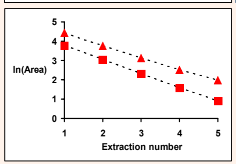


Fig. 6. Linearity of semi-logarithmic plot is very good demonstrating exponential behavior. r^2 = 0.9998 and 0.9999, respectively

Measurements performed on HP6890 GC with CombiPAL sampler. Polyvinyl pyrrolidone bound 5-amino salicylic acid (5-ASA) granulate samples (50mg in 10ml sample vials) are spiked with acetone and 2-propanol dissolved in methyl *tert*-butyl ether. Prior to headspace sampling the samples are heated for 20min @ 80˚C.

MHE theory and results

With an equilibrium beetween the headspace and the condensed sample, the measured signal is
$\mathbf{A_i = A_0*exp(-k*i)}$ and the total signal is $\mathbf{A_{tot} = \Sigma_{i=0}^{\infty} A_i}$
The total signal can be calculated as $\mathbf{A_{tot}=A_0/(1-exp(-k))}$
$\mathbf{A_0}$ and $\mathbf{k}$ are determined from the semilog-plot.
The amount of analyte in the sample is $\mathbf{A_{tot}}$
The fraction of sample analyte that is removed from the vial during each extraction step is **1-exp(-k)** This is the depletion factor.
As shown in Table 1 the depletion factor is very uniform, confirming that the syringe sampling is well-controlled.

Table 1. Repeatability and depletion data from repetitive measurements on the CombiPAL sampler. Set of 8 samples.

	acetone (ug)	2-propanol (ug)	depletion acetone	depletion 2-propanol
MEAN	8.78	20.10	0.508	0.474
SDEV	0.90	1.45	0.0020	0.0032

Comparison of syringe *vs.* loop based sampling and of various vials/caps/septa combinations

The loop-based sampler is often employed for MHE measurements. Table 2 shows recoveries from sets of four identical samples ran on the two sampler systems.

Table 2. Data from CombiPAL syringe *versus* HP/Agilent 7694 loop-based sampler. From sets of 4 identical samples.

	acetone (ug)		2-propanol (ug)	
	CombiPAL	HP7694	CombiPAL	HP7694
MEAN	9.53	8.76	21.2	21.8
SDEV	0.28	0.29	0.49	0.44

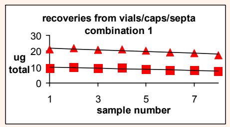


Fig. 7. Recoveries as a function of the sample number. "Late" extractions obviously yield lower recoveries (data from CombiPAL).

■ acetone
▲ 2-propanol

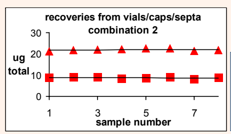


Fig. 8. Recoveries by sample number. The recoveries are constant (data from loop sampler).

Vial combination 1: 10ml screw top vials
Vial combination 2: 10ml crimp top vials.

Discussion and conclusion

It has been demonstrated that the Multiple Headspace Extraction technique (MHE) can be applied as a new technique to enhance the versatility of the syringe-based CombiPAL autosampler.

Results compare well between the CombiPAL and the loop-sampler with both methods showing recoveries of around 90%.

Loss of sample through the septum can be a major cause of error in MHE. Processing times for series of samples are often quite long, and samples at the end of a series can suffer from loss of sample depending on the combination of vials/caps/septa used.

Loss rates in far excess of 3% have previously been reported (ref. 1). These data indicate that the combination of vials and caps can have a profound influence on the results obtained by headspace sampling, be that with syringe sampling or loop sampling. The preliminary data (to Be published) show the influence of the vial-cap-septa combination resulting in big differences of loss of analyte.

Literature

1) Baltensperger, B. 2003. Vials, Caps, Septa & Various Products in Comparison. Application note #02, CTC Analytics AG.
2) Kolb, B., and Ettre, L.S. 2006. Static headspace-gas chromatography, theory and practice. Wiley-Interscience.

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