ARGENTATION BASED (MEPS) FOR THE ANALYSIS OF FAMES BY GCMS

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Introduction

Micro Extraction by Packed Sorbent (MEPS) is an adaptation of SPE that incorporates all the desirable characteristics into a miniaturized device with a typical void volume of less than 10 µL. With operating volumes of this scale and its compatibility with autosampler syringes, MEPS allows the specificity of the solid-phase process to be harnessed for digital chromatography using discontinuous changes in solvent polarity (Fig 1). The eluant volumes are sufficiently small to be injected directly into a GC with a large volume injector or, alternatively, subsampled into a conventional split/splitless injector and therefore MEPS can be used as a digital LC - elution GC approach to analysis.

In this application, we use the selectivity of an argentation sorbent to speciate a mixture of fatty acid methyl esters on the basis of unsaturation in the first dimension and then to separate groups by conventional non-polar GCMS in the second dimension.

Material and methods

A SCX (propylsulphonate modified silica) MEPS cartridge (SGE Analytical Science) was conditioned with 200 µL of a mixture of 8 % w/v silver nitrate in acetonitrile-water (10:1). The sorbent was then washed sequentially with acetonitrile (200 µL), acetone (200 µL) and dichloromethane (200 µL).

A 37 FAME standard and a PUFA FAME standard (Fig 2) (Supelco Inc., Bellefonte, USA) were mixed in a ratio of 1:1 in dichloromethane and a 50 µL portion of the sample was drawn through the sorbent bed then expelled at a flowrate of 10 µL/sec. The sorbent was washed with dichloromethane-hexane (2 x 100 µL) and then eluted sequentially with dichloromethane (2 x 50 µL), acetone (2 x 50 µL) and acetone-acetonitrile (94:6, 2 x 50 µL). Eluted fractions from the MEPS column were sampled into the GC injection port.

Gas Chromatography Mass Spectrometry was performed on a 6890GC-5973N MSD (Agilent Technologies, Palo Alto, USA) equipped with an ETP electron multiplier and a BPX5 column (30 m x 0.25 mm i.d., 0.25 µm film thickness, SGE Analytical Science). Injections of 1 µL were fast and splitless at 250 °C with a purge flow of 50 mL/min and a nominal inlet pressure of 0.7 psi. The oven temperature was initially 40°C and ramped at 20 °C/min to 350 °C then held for 2 minutes. The carrier gas was helium at a flow rate of 0.5 mL/min in constant flow mode. EI mass specta were collected over the range 50-550 Da. The quadrupole temperature was 150 °C and the source was 230 °C.

The method is used here in a decoupled mode but was also suitable for coupled analysis from the MEPS cartridge directly into a PTV equipped injector with elution volumes of 10-20 µL for each fraction. The MEPS cartridge was cleaned between analyses by washing with acetonitrile and dichloromethane. The metal construction of the MEPS cartridge prevented photo-oxidation of the silver and the sorbent remained stable in its silver-ion form for in excess of 24 hours.

Results and discussion

Argentation media (e.g. propyl-$SO_3^-Ag^+$) have a high surface polarity generated by the ionic double layer of ion exchanger and silver cations (Fig 3) and so their retention of organic compounds may be rate limited relative to other solid-phase mechanisms. However, selectivity towards unsaturation in combination with low Van der Waals capacity means that argentation can be used to speciate on the basis of unsaturation. These normal phase characteristics make argentation a useful digital technique that uses solvents that are compatible with GC inlets.

Argentation is useful for the speciation of fatty acid methyl esters (FAME) mixtures in which unsaturated target analytes may be swamped by more abundant saturated FAME. To demonstrate the technique it was applied to complex mixtures of saturated and unsaturated FAME compounds. FAME with two or more double bonds were separated from saturated and mono-enic analogues. Saturated and monoenic FAME were recovered without retention, dienic and trienic FAME were eluted with some more unsaturated FAME and finally the polyenic FAME was completely eluted by the inclusion of 6 % acetonitrile to completely disrupt the silver ion-enic complexes (Fig 4). Elution solvents were suitable for GCMS (dichloromethane, acetone and acetonitrile) and volumes were small enough for direct injection or subsampling without prior concentration.

Conclusion

An Ag^+-MEPS-GCMS method has been developed for the analysis of complex FAME samples. The technique generates a three dimensional array of chromatographic data by sequential analysis of discrete MEPS fractions.

Because the MEPS method is based on either strong retention or full elution of particular groups, the cartridge can be 'parked' with solvent while each GC run is under way. The incorporation of sample preparation into the chromatographic method not only allows for a greater degree of automation in sample processing but also realizes the untapped information content of a selective sample preparation scheme in such a way that it can be included in the data set as a discrete dimension.

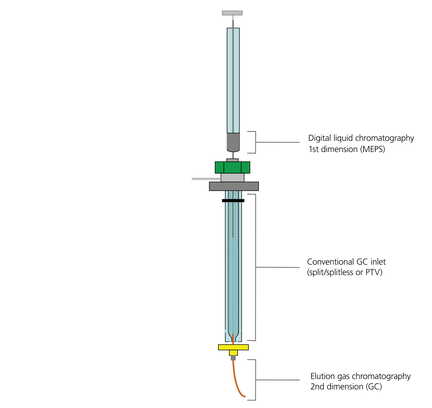

Figure 1: A MEPS approach allows a digital-LC dimension to be interfaced via a conventional GC injection port to an elution GC dimension (or dimensions) to produce an array of second dimension chromatograms.

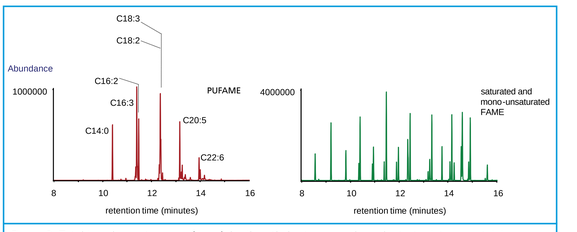

Figure 2: Total ion chromatograms for a fish oil methyl esters sample and a test mixture containing mono-ene and saturated fatty acid methyl esters.

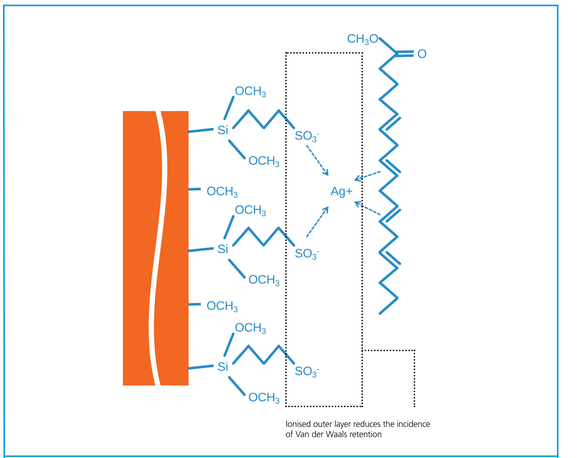

Figure 3: Argentation chromatography on a propylsulphonate modified silica sorbent occurs on a highly polar (ionic) surface and so has a relatively low capacity for non-polar organic analytes. The secondary retention mechanism of van der Waals interactions with the propyl moieties is sterically hindered by the ionic layer.

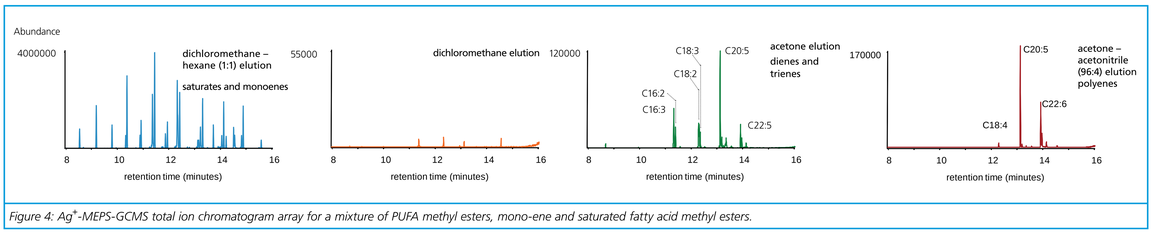

Figure 4: Ag^+-MEPS-GCMS total ion chromatogram array for a mixture of PUFA methyl esters, mono-ene and saturated fatty acid methyl esters.

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