# THE INTEGRATION OF MICROEXTRACTION PACKED SORBENT (MEPS) INTO MULTIDIMENSIONAL STRATEGIES

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## Introduction

LC-GC approaches to analysis are particularly attractive because they combine the selectivity of solid-phase sorbents in the first dimension with the separating power and peak capacity of a capillary GC column in the second and subsequent dimensions. Widespread use of the technique is limited because of the difficultly in desolvating the stream from the LC dimension without the solvent vapour passing down the GC column in significant quantity.

An alternative approach to elution chromatography in the first dimension is to harness the specificity of the solid-phase process for digital chromatography using discontinuous changes in solvent polarity (Fig 1). Digital chromatography on a small sorbent bed reduces the volume of mobile phase to discrete plugs that are sufficiently small to be injected directly into a GC with a large volume injector or, alternatively, subsampled into a conventional split/splitless injector.

Microextraction 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, the MEPS format is the ideal for 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.

## Experimental detail

A  SCX MEPS cartridge (propylsulphonate modified silica, 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 (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 (GCMS) was performed on a 6890GC-5973N MSD (Agilent Technologies, Palo Alto, USA) equipped with an ETP 14642 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 quadrapole 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.

## Results and Discussion

By necessity, 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 2). While such surfaces are wettable by aqueous samples, extraction of essentially non-polar analytes from organic solvents may be rate limited and the sorbent capacity lower than is observed for other solid-phase mechanisms. However, the selectivity of the sorbent towards unsaturation in combination with its very low van der Waals capacity means that it can be used to speciate compounds of interest on the basis of degree of unsaturation (Fig 2).  These normal phase characteristics make argentation a useful digital chromatographic technique because it uses solvents that are compatible with GC inlets.

Argentation is particularly useful for the speciation of fatty acid methyl esters (FAME) mixtures in which unsaturated target analytes may be swamped by more abundant saturated FAME. As a test of the technique, known FAME mixtures (Fig 3) were mixed in equal proportion to give a complex mixture of saturated and unsaturated compounds. When applied in MEPS format, the argentation technique allows the separation of FAME with two or more double bonds from saturated and mono-enic analogues (Fig 4). Elution is with solvents that are suitable for GCMS (dichloromethane, acetone and acetonitrile) and in volumes that are small enough for direct injection or subsampling without prior concentration.

In the application, shown in Fig 3, saturated and monoenic FAME was recovered without retention, dienic and trienic 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-ene complexes.

## 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 or without solvent while each GC run is under way. The incorporation of sample preparation into the 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.

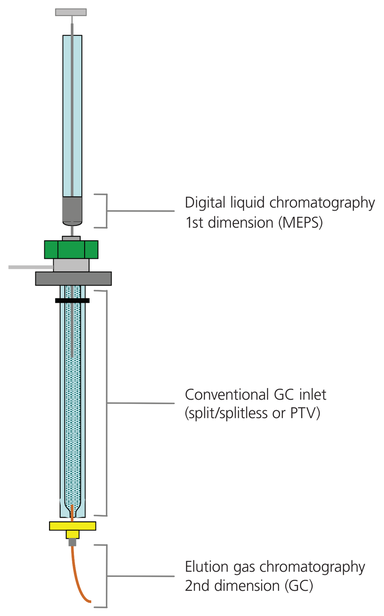


*Figure 1:  A MEPS  approach allows  a digital-LC dimension to be interfaced via a conventional GC injection port to an elution GC dimension (or dimensions) to produce an array of second dimension chromatograms.*

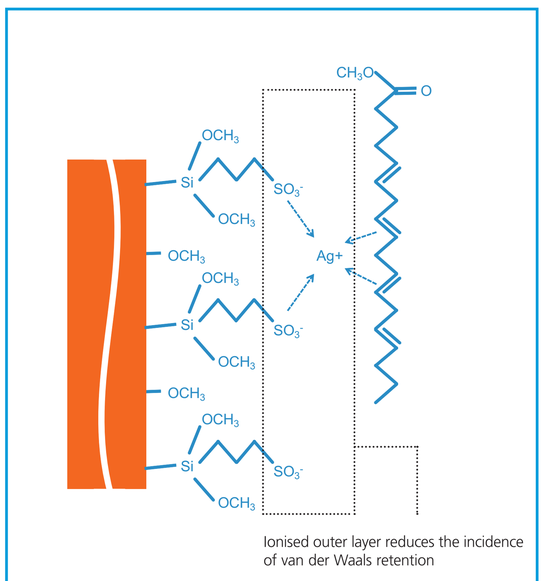


*Figure 2: Argentation chromatography on a propylsulphonate modified silica sorbent occurs on a highly polar (ionic) surface and so has a relatively low capacity for non-polar organic analytes. The secondary retention mechanism of van der Waals interactions with the propyl moieties is sterically hindered by the ionic layer.*

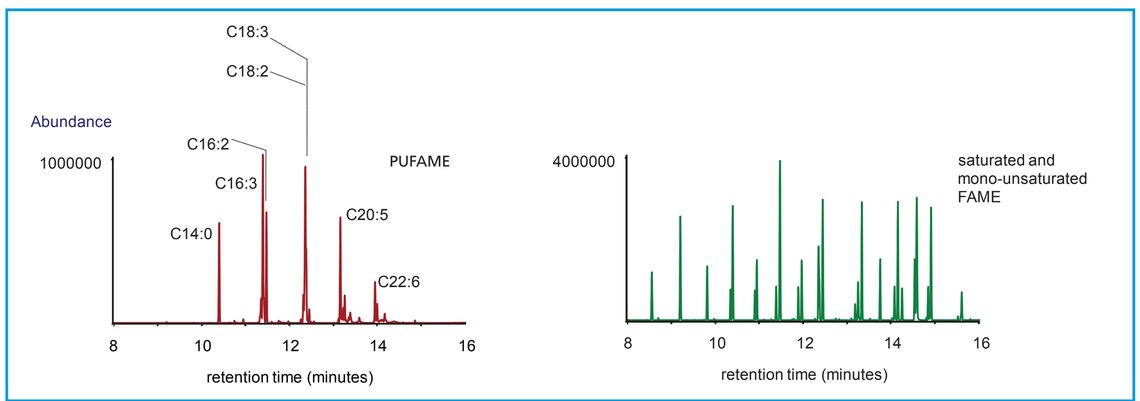


*Figure 3: Total ion chromatograms for a fish oil methyl esters sample and a test mixture containing mono-ene and saturated fatty acid methyl esters.*

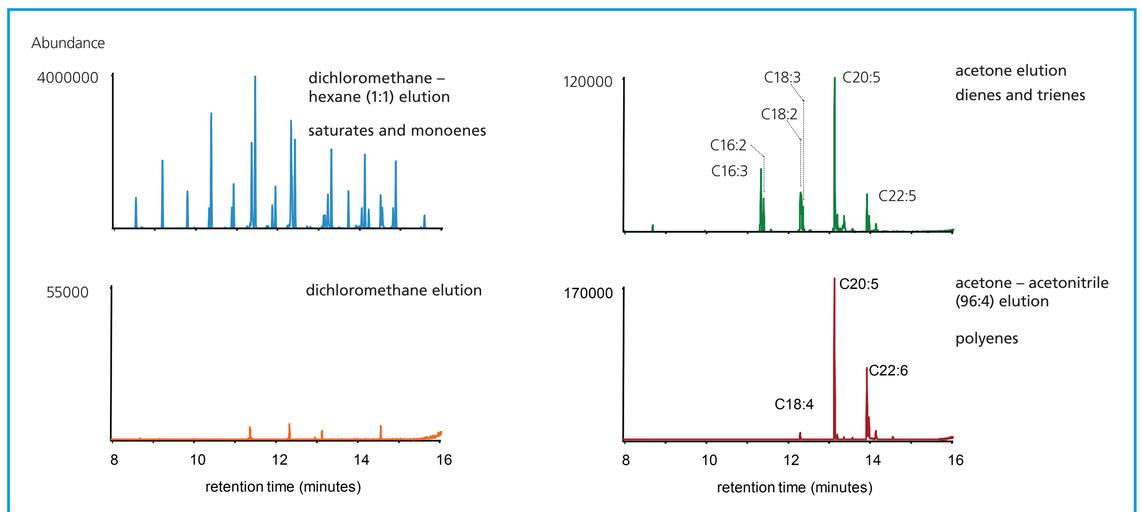


*Figure 4: $Ag^+$-MEPS-GCMS total ion chromatogram array for a mixture of PUFA methyl esters, mono-ene and saturated fatty acid methyl esters.*