MICRO EXTRACTION PACKED SORBENT (MEPS): ANALYSIS OF FOOD AND BEVERAGES

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Introduction

MEPS is a development of conventional SPE that has miniaturised the sorbent bed so that it can be incorporated into the sample path without voids. Typically, a MEPS method reduces sample and reagent consumption by several orders of magnitude over conventional methods. Extraction performance is comparable to conventional SPE because the MEPS sorbent bed retains the same dimensional ratios of the conventional device and adaption of existing methods is achieved by scaling all steps in proportion to the bed volumes (typically 1 mL for SPE and 10 µL for MEPS). The small scale of the MEPS device allows elution in a small volume and so the entire extract may be analyzed rather than only using a portion of the prepared extract in a conventional experimental design. SPE and MEPS are not the same as SPME or SBSE techniques. The former rely on solvent desorption and use a mono-layer extraction surface with a very large surface area. The latter are immobilised liquid extraction techniques that are typically used in thermal desorption mode.

Discussion

The retention of analytes in liquid chromatographic methods using solid sorbents is described in terms of elution volumes (V) and partition coefficent for the analyte, sorbent and mobile phase (K) using the equation:

$$V_r = V_m + KV_s$$

For combinations in which K << 0.2 or K >> 200, retention characteristics are considered to be unsitable for elution chromatography with retention been either too little or too great for practical method development. SPE utilises this region of chromatographic properties in combination with abrupt changes in solvent composition to achieve either complete retention or complete elution. This form of discontinuous sorption is refered to as digital chromatography and typically relies on sorbent selectivity rather than efficiency for separation. Unlike elution chromatography, diffusion into and out of the sorbent (radial flowrate) is rate limiting over axial flowrate for SPE and, accordingly, the ideal method is based on a column with one theoretical plate.

The advantages of MEPS are realised on the basis of this theory. Because SPE methods are rate limited on flowrate, increased throughput using existing sorbents is only possible by reduction in scale. Thus, for a 5 mL sample processed through a conventional device it is typical that delivery of sample and reagents will take 9 minutes at a flow rate of 1 mL/min. Scaling the method to achieve the same concentration factor on a MEPS device allows liquid delivery to occur in 0.75 minutes. Processing of the unscaled sample on a MEPS device can occur in a time comparable to the conventional SPE approach (10 min) but with an increase in concentration factor from 5:1 to 25:1.

Reducing the scale of sample extraction is important in reducing consumption and waste disposal costs but also offers the opportunity to prepare a sample on a scale that is compatible with the sample size limits of chromatographic inlets and in realtime with GC or LC instrumentation. Meeting these two requirements make MEPS suitable for the on-line adaption of solid-phase methods into GC and LC autosamplers.

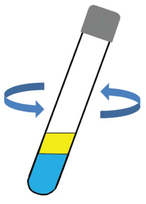
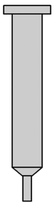
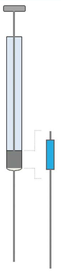
In the areas of food and beverage analysis, published applications describe MEPS for the analysis of bio-flavonoids from red wine, diterpene glycosides from tea extract, pesticides and PCB in fats, aflatoxin B2 and M2 metabolite trace analysis in milk, mycotoxin trace analysis in cereal, fatty acid methyl esters (long chain) in fermentation medium, omega-6 fatty acid in malt lipid, pigment anthocyanidins in wine, atrazine in cereal, sulfonamide trace analysis in meat, penicillin in dairy products and cork taints in wine.

Multi-eluate strategies for speciation of fatty acids methyl esters using argentation-MEPS and solvent selective reversed-phase speciation of seed extracts on C2 sorbents have also been reported for GCMS.

As well as adaptation to chromatographic methods, MEPS is also suitable for modification of the selectivity of immunoassay performance and can be adapted to 96 well platforms. Extending our previous work in this area, sensitivity and selectivity improvements can improve detection limits by more than an order of magnitude by reducing the contribution of the matrix background.

Conclusion

MEPS is presented as an integrated SPE cartridge and gas-tight syringe for micro-scaled sample preparation. The hardware is suitable for manual use or may be deployed on a CTC autosampler using a commercially available package that includes conflict free software to control the sampler work surface. When coupled with an autosampler, MEPS is suitable for true on-line SPE analysis using GC and LC plaforms.

LIQUID-EXTRACTION	SOLID-PHASE EXTRACTION	MEPS EXTRACTION
		
Difficult to automate	Automation available	Automation possible
Standalone methods	Difficult to put on-line	Designed for on-line use
Emulsions	No emulsions	No emulsions
Labour intensive and relatively slow	Parallel operation gives high throughput	Low volumes gives a fast method
Polar compounds difficult to extract	Polar and charged compounds may be extracted	Polar and charged compounds may be extracted
High solvent useage	Moderate solvent useage	Low solvent useage
Depleted sample may be solvent contaminated	Depleted sample may be recovered uncontaminated	Depleted sample may be recovered uncontaminated

Wine and other beverages

On-line C18 MEPS – LCMS or GCMS for bioflavanoids in red wine
Sample in water (red wine)
Elution with methanol
App. A-05, SciSEP Accurate Science, On-line MEPS Kit, 2008.

On-line C18 MEPS – LCMS for diterpene glycosides in black tea
Sample in water (tea)
Combined sequential elution with methanol and methanol-acetonitrile (1:1)
App. A-11, SciSEP Accurate Science, On-line MEPS Kit, 2008.

C18 MEPS - GCMS for trichloro- and tribromoanisole taints in wine.
Sample in water (wine).
Elution with toluene with methanol wash.
Jönsson S, Hagberg J, Lahoutifard N, Wynne P, Van Bavel B. MEPS: A new technique for the analysis of small brominated and chlorinated aromatic compounds in wine, Trends in Food Analysis VI, Belgium 2009.

Milk

C18 MEPS – ESI-MS for penicillin and streptomycin in milk
Sample in milk
Sequential elution with aqueous acid (pH 2) and methanol
Melville D, Wirth HJ, Wynne PM, unpublished results, SGE Analytical Science, Ringwood, Australia.

Fish and oil samples

Ag+ MEPS - GCMS for separation of fish oil FAME based on degree of unsaturation
Sample in hexane-dichloromethane
Sequential elution with dichloromethane, acetone and dichloromethane – acetonitrile
Dawes P, Dawes E, Wynne PM. On-line and off-line application of micro-SPE, Australasian AOCS Conf., Werribee, Australia, Oct 31-Nov 1, 2006.

C2 MEPS - GCMS for separation of FAME and other components from seed meal
Sample in water-methanol-ammonia (90:9:1)
Sequential elution with hexane, dichloromethane, methanol
Hibbert R, Lahoutifard N, Wynne PM. Argentation based MEPS for analysis of FAMES by GCMS, Trends in Food Analysis VI, Belgium 2009.

On-line C18 MEPS – GCMS for FAME in fermentation medium
Sample in hexane-tertiary butyl ether (1:1)
Elution with dichlormethane
App. F-04, SciSEP Accurate Science, On-line MEPS Kit, 2008.

Cereal grains

On-line C18 MEPS - LCMS for F-2 mycotoxin on corn
Sample in water-methanol (2:1).
Elution with methanol-water (70:30)
App. F-03, SciSEP Accurate Science, On-line MEPS Kit, 2008.

On-line C18 MEPS - LCMS for atrazine in ground corn
Sample in water-methanol (2:1).
Elution with methanol
App. F-07, SciSEP Accurate Science, On-line MEPS Kit, 2008.

C8/SCX MEPS - GCMS for opiate contamination of oats and animal feeds
Sample in neutralised aqueous extract or diluted ammoniated methanol extract
Elution with dichloromethane-isopropanol-ammonia (50:50:2)
Wynne PM, Dawes PA. GCMS in forensic drug analysis: application to opium contaminated animal feeds, Pittsburgh Conference, Orlando, USA, March 12-17, 2006.

Meat residues

On-line C8/SCX MEPS - LCMS for sulphonamide drugs in meat
Sample in acetone-chloroform-acetic acid (10:10:1)
Elution with methanol-ammonia solution.
App. F-08, SciSEP Accurate Science, On-line MEPS Kit, 2008.

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