Monitoring water quality by passive sampling and GC×GC–TOF MS with variable-energy electron ionisation

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Introduction

Two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC–TOF MS) can provide highly sensitive detection and confident mass spectral identification of pollutants within complex environmental extracts. Nevertheless, the identification of individual compounds may be hindered by weak molecular ions or when similar mass spectral characteristics are evident across entire chemical classes. Select-eV ion source technology aims to combat this problem by allowing both hard and soft electron ionization with no inherent loss in sensitivity.

The routine monitoring of water quality is now a requirement of environmental legislation, such as the EU's Water Framework Directive. Often the cause of poor water quality is unknown, and extensive investigative monitoring is needed to determine what chemical may be responsible. In this study, we investigate the parallel between passive sampling devices in river courses and silicon prostheses in the human body for the concentration of environmental contaminants. This novel approach aims to better estimate the overall body burden of bio-accumulative substances and how this changes over time of exposure.

This poster shows the suitability of this analytical platform for environmental investigations, using both target-focused studies as well as non-targeted routines for screening for the presence of emerging contaminants in two complex matrices.

Sample preparation

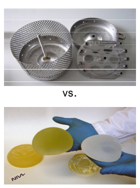


Figure 1: Semi-permeable membrane device (SPMD, top) and explanted silicon breast prosthesis (bottom).

Passive sampling devices (*e.g.* semi-permeable membrane devices (SPMDs), LDPE and silicone rubber) are often used for monitoring water quality. The samplers were deployed for several weeks in a polluted river course in the UK to effectively sequester large volumes of water and provide a concentrated, representative extract for analysis by GC×GC–TOF MS. Passive samplers enable minimal sample preparation, this minimising the loss of possible compounds of interest. Full experimental details for the collection and preparation of water samples have previously been reported.[1]

Three removed implant samples (as well as a new prosthesis as the control blank) were extracted through MeOH–water (80:20 v/v; 300–400 mL) into cyclohexane in 2 L beakers (Figure 2). Extraction using 200–300 mL cyclohexane was repeated twice over the course of a week. The cyclohexane phases were then combined and reduced to 2 mL and spiked with an internal standard mix (100 ng of CB-30, CB-53 and CB-204).

For this study, a 0.5 mL aliquot was exchanged to methanol and diluted with water. Compounds were then picked-up with clean silicone rubber (AlteSil, 2–4 g). The silicone rubber was then extracted with cyclohexane and reduced.

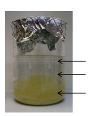


Figure 2: Extraction of compounds of interest from a silicon breast prosthesis.

1 A. Gravell *et al.*, GC×GC–TOF MS complements passive sampling for the screening of pollutants in water, *LCGC: Current Trends in Mass Spectrometry*, March 2013, pp. 8–14.

Experimental

A BenchTOF-Select™ time-of-flight mass spectrometer (Markes International) was used for all analyses, in combination with a GC×GC gas chromatograph (Agilent 7890 GC with Zoex ZX1 modulator).

Figure 3: BenchTOF-Select with GC×GC.

Injection: PTV inlet splitless mode. Inlet temperature 250°C (hold 1.2 min), 720°C/min to 300°C.

GC×GC: Column set: BPX5 (30 m × 250 µm × 0.25 µm) and BPX50 (3 m × 100 µm × 0.10 µm). Oven: 65°C for 2.0 min, then 5°C/min to 315 °C (hold 5 min). No secondary oven offset. Modulation time: 4 s. Hot-jet pulse: 350 ms.

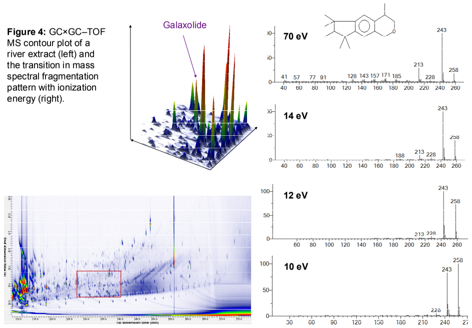
BenchTOF-Select: 50 Hz; mass range: m/z 40–500; ion source: 250°C; transfer line: 300°C.

Analysis of contaminated river water

Initial studies focused on the analysis of environmental contaminants in a UK river using an SPMD extract run at various ionization energies. It was discovered that, for the majority of compounds, optimal sensitivity was achieved at 12–14 eV. In the example shown in Figure 4, the mass spectrum for galaxolide (a polycyclic musk commonly found in cosmetics) changes significantly with ionization energy.

Select-eV provides enhanced molecular ions whilst retaining structurally-significant fragment ions, delivering both confident compound identification and increased selectivity.

Figure 4: GC×GC–TOF MS contour plot of a river extract (left) and the transition in mass spectral fragmentation pattern with ionization energy (right).



Analysis of breast implants

In a second study, silicone breast prostheses obtained from patients over a wide age range were collected. Silicone oils in the prosthesis extracts were removed using the described multi-step extraction procedure, and the resultant extracts were analysed by GC×GC–TOF MS with Select-eV.

The analysed extracts were extremely complex (Figure 5), and contained a range of compound types, including pharmaceuticals, hormones and persistent organic pollutants (POPs).

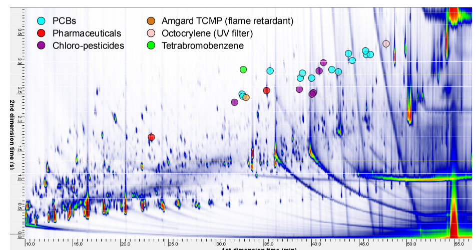


Figure 5: GC×GC–TOF MS contour plot of an explanted silicon breast prosthesis extract.

Pharmaceuticals

Lidocaine (a common painkiller) and Propofol (an analgesic) were detected in one of the prosthesis extracts. Select-eV ionization (14 eV) improved the absolute abundance of the molecular ion in both cases, leading to improved limits of detection (Figure 6).

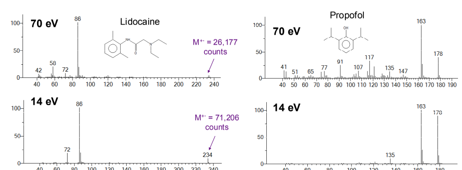


Figure 6: Mass spectra for two pharmaceuticals, acquired at 70 eV and 14 eV using Select-eV.

Persistent organic pollutants (POPs)

A number of POPs were detected in the explanted breast prostheses, including numerous PCBs (Figure 7), as well as several chlorinated pesticides, such as *p,p'*-DDE. An ionization energy of 14 eV enabled greater selectivity for such compounds by reducing spectral fragmentation (Figure 8).

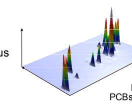


Figure 7: GC×GC surface plot showing a range of PCBs in an explanted breast prosthesis extract (summed EIC m/z [256 + 292 + 326 + 360 + 394 + 430]).

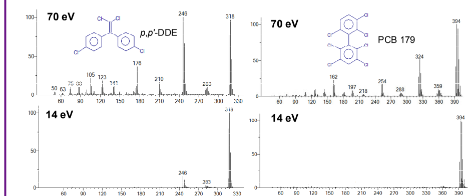


Figure 8: Mass spectra for two POPs, acquired at 70 eV and 14 eV using Select-eV.

The GC×GC plot of the control extract prepared using a new prosthesis was surprisingly complex (Figure 9), containing aliphatic compounds and numerous PAHs (but none of the POPs or pharmaceuticals detected earlier). A possible explanation for this is that the prosthesis is sampling chemicals from the air, indicating that storage conditions should be rigorously controlled in future studies.

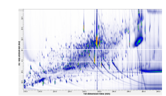


Figure 9: GC×GC–TOF MS contour plot of a new prosthesis extract.

Conclusions

We have shown in this poster that GC×GC–TOF MS is an ideal choice for the analysis of complex extracts from breast implants, and that Select-eV greatly improves screening capabilities, by simplifying targeted spectra and increasing both sensitivity and selectivity.

In addition, we have identified this approach as a step towards achieving better understanding of the overall body burden of bio-accumulative substances, and how this changes with time.

Future studies will focus on quantitative extraction of targets from the implant samples, to better gauge their health impacts and allow levels in the body and environmental matrices (*e.g.* drinking water) to be compared.

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