Use of Q-TOF GC/MS to quantify SPMD extracts from river water and marine sediment

Sofia Aronova[1], Anthony Gravell[2]   (1) Agilent Technologies, U.S.A.; (2) 'National Laboratory Service, Llanelli Laboratory, Environment Agency (England & Wales)

Agilent Technologies

Introduction and Experimental

Introduction
Surface water quality is vitally important to our everyday life. Protecting such a valuable resource requires chemical testing typically involving mass spectrometric analysis. However, extracts from river water, waste water and marine sediments using GC/MS generates a large number of unknown compounds that need to be identified and subsequently quantified. In principle, MS can used to elucidate the *de novo* structure of unknown compounds beginning with the determination of molecular formula of the molecular ion, using accurate mass measurements that have errors less than a few parts per million (ppm). Mass measurements obtained with errors below 2 ppm combined with the isotopic distribution of the mono-isotopic peak can be used to eliminate many of the possible molecular formulae.

The complex organic matrix found in sediment samples makes the identification and quantification by low resolution MS difficult. This poster demonstrates the use of exact mass measurement using a Q-TOF GC/MS to identify and quantify several classes of pollutants commonly found in marine sediment and river water.

Materials
Standard solutions of various classes of compounds including Polyaromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polybrominated Diphenyl Ethers (PBDEs), Organo-chlorine Pesticides (OCP) and Polycyclic Musk Fragrances (PCMs) together with extracts from passive samplers (SPMDs) and solvent extracts from marine sediments (NIST SRM 1944b) were also analyzed in scan mode and in MS/MS mode.

Chromatography
Column	30 m x 0.25 mm x 0.25 µm
	DB5-ms Ultra Inert (122-5532UI)
Carrier gas	Helium
Carrier gas flow	2.9 mL/min
Injection port	Multimode Inlet (MMI), air cooled;
MMI temperature program	60˚C (0.35 min) – 900 (1 min)
Split mode	Splitless
Injection volume	1 µL
Liner	Deactivated 2 mm dimpled single taper splitless
Oven program	70˚C (2 min); 25˚C/min to 150˚C;
	3 ˚C /min to 200˚C; 8˚C/min to 280˚C (10 min)

Mass Spectrometry
Accurate mass measurements were obtained with an Agilent 7200 Q-TOF GC/MS instrument (Figure 1) using a 4-GHz dual gain analog-to-digital converter (ADC) data acquisition option. Typical mass resolution of >13,000 and mass accuracy <2 ppm were routinely achievable. Mass calibration utilized PFTBA (perfluorotributylamine). A second compound with fewer masses can be used as an internal reference mass (IRM) to increase mass accuracy and to correct for small changes in the mass calibration over long time intervals. PFET (pentafluoro-ethyl triazine), was used in this study for the IRM.

The 7200 has three differentially pumped sections (Figure 2) with the pressure in the flight tube being less than 10^{-8} Torr. The EI or CI ion sources can be removed and changed without venting the mass analyzer region. The ion source is located in a separate chamber than can be isolated from the main vacuum chamber by an isolation valve.

Agilent's MassHunter Workstation software was used for quantification and to generate molecular formulas from exact masses of the monoisotopic peaks and to validate them using isotope distributions of the molecular and major fragment ions.

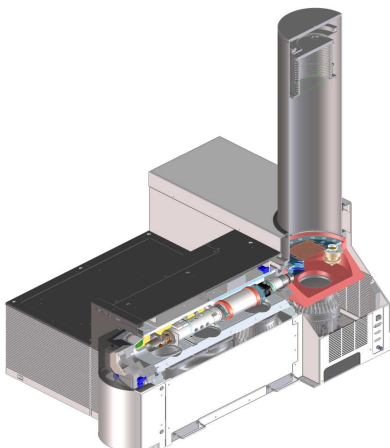|	
Interface temp	290 ˚C
Source temp	230 ˚C
Quadrupole temp	150 ˚C
Scan range	m/z 40-800
ADC rate	4 GHz
Net data rate	5 Hz

Figure 1   Agilent 7200 Q-TOF GC-MS

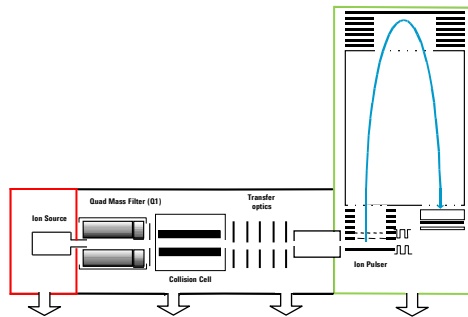## Quantitation & Mass Accuracy

Figure 2   Agilent 7200 Q-TOF GC/MS

Calibration Curves
Figure 3a shows the TIC of 0.61 ppm Hexachlorobenzene in a SPMD extract of river water with a scan range 40-800 Da. and scan rate 5 Hz. Figure 3b shows the EIC for m/z 283.8096 using an extraction window of +/- 0.5 Da., which represents the performance of a low resolution single quadrupole MS. An extraction window of +/- 2 ppm (0.57 X 10^{-3} Da.) is shown in Figure 3c and demonstrates the advantage high resolution, accurate mass for reducing the interferences from the chemical matrix.

The ability to eliminate chemical matrix interferences improves quantitation and the use of a high speed dual gain ADC provides a large dynamic range. Typical calibration curves for standards are shown in Figure 4a and 4b for the compounds Acenaphthylene (0.2-1000 ppm) and Hexachlorobenzene (1 ppb-5000 ppb). Linear ranges of about four orders of magnitude or more are typical depending on the scan conditions, mass range scanned and the number of transients averaged.
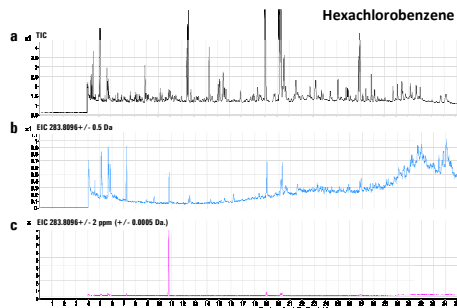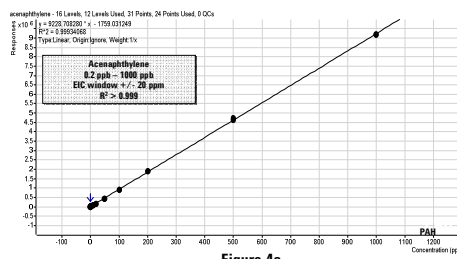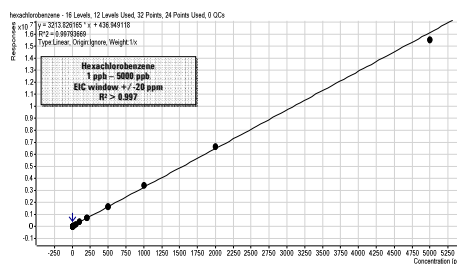

Figure 3

Figure 4a

Figure 4b

Mass accuracy
Typical mass accuracy uncorrected (without using internal reference mass - IRM) and corrected (with IRM) are shown if TABLES I and II for concentrations of 100 ppb and 0.5 ppb. The mass accuracy diminishes at lower concentration due to the smaller number of ions in the chromatographic peak and the accompanying larger statistical fluctuation of the signal, which increases the measurement error of the mass centroid. In addition to an increased linear response range for quantitation, the other advantage of ADC based signal detection is a larger range over which accurate mass is maintained.

Results and Discussion

TABLE I

Standard solution 100 ppb	Molecular formula	Exact mass	Mass error (ppm)	Mass error (ppm)
fluorene	C13H10	165.0699	5.452235689	0.605803965
hexachlorobutadiene	C4Cl6	224.8408	4.447591362	0.889518273
hexachlorobenzene	C6Cl6	283.8096	3.875837886	0.704697797
dieldrin	C12H8Cl6O	262.8564	2.282615147	-1.521743431
BZ # 52 (2,2',5,5' - tetrachlorobiphenyl)	C12H6Cl4	291.9189	2.740487169	-0.342560896
BDE-47_1	C12H6Br4O	485.7106	0.205883915	-2.470606983
DPMI (Cashmeran)	C14H22O	191.143	3.662179625	-0.523168518
HHCB (Galaxolide)	C18H26O	243.1743	2.056138334	-0.822455333
Average			3.090	0.985
			uncorrected	corrected

TABLE II

Standard solution 0.5 ppb	Molecular formula	Exact mass	Mass error (ppm)	Mass error (ppm)
fluorene	C13H10	165.0699	-12.11607931	-3.634823793
hexachlorobutadiene	C4Cl6	224.8408	-3.113313954	-1.334277409
hexachlorobenzene	C6Cl6	283.8096	-9.161071366	-3.875837886
dieldrin	C12H8Cl6O	262.8564	-6.467409582	-6.086973724
BZ # 52 (2,2',5,5' - tetrachlorobiphenyl)	C12H6Cl4	291.9189	-8.564022405	-4.110730754
BDE-47_1	C12H6Br4O	485.7106	4.941213966	4.32356222
DPMI (Cashmeran)	C14H22O	191.143	-1.046337036	3.662179625
HHCB (Galaxolide)	C18H26O	243.1743	0	0
Average			4.151	2.992
			uncorrected	corrected

Limit of quantitation
This was a preliminary study to evaluate the suitability of using a Q-TOF GC/MS for confirming and quantifying a broad range of chemical classes of pollutants commonly found in marine sediment and extracts from passive samplers (SPMD) deployed in rivers. This required a preliminary assessment of instrument operating conditions appropriate to reduce chemical matrix interferences, maximize linearity, achieve a high degree of confirmation and obtain the desired limit of quantitation. Table III shows measurements of PAH's in SPMD extracts deployed in a river in the United Kingdom and a waste water drain. The limits of quantitation shown in Table III were estimated by determining the sample amount at which the measure response deviated from the calibration curve by 20%. Limits of quantitation for PAH's are typical and were lower than any of the observed compounds in the actual samples. The detection limit (3 X N_{RMS}) for benzo(a)pyrene was 0.5 ppb and close to the maximum contaminate level (MCL) limit of 200 ng/L (0.2 ppb) for Benzo(a)pyrene recommend by the U.S. EPA[1].

TABLE III

Location		Waste Water	SPMD River Extract	
Analyte	Quant Ion	Total analyte per SPMD (ug/SPMD)	Estimated water concentration (ng/L)	Estimated Limit of Quantitation (ppb)
Acenaphthene	152.0621	17.3	2.2	5
Phenanthrene	178.0777	90.5	25.3	< 1
Anthracene	178.0777	16.6	5.0	10
Fluoranthene	202.0777	53.5	75.5	5
Pyrene	202.0777	41.2	57.5	5
Benz[a]anthracene	278.109	18.5	10.2	< 1
Benzo[b]fluoranthene	252.0934	46.5	ND	< 1
Benzo[k]fluoranthene	252.0934	17.1	3.0	< 1
Benzo[a]pyrene	252.0934	4.0	3.0	50
Benzo[ghi]perylene	276.0934	ND	3.4	5
Fluorene	166.0777	22.6	3.4	<1
Indeno Pyrene	276.0934	3.4	ND	2
Chrysene	228.0934	ND	18.5	100

Conclusions and Future Studies
Reported here are the results of a preliminary assessment of the suitability of using a Q-TOF GC/MS for confirming and quantifying a broad range of chemical classes of pollutants commonly found in marine sediment and river water. Instrument operating conditions were established that were appropriate to reduce chemical matrix interferences, maximize linearity, achieve a high degree of confirmation and obtain the desired limit of quantitation.

The identification and quantification was demonstrated by means of high resolution and accurate mass measurements. The availability of standards is required to unequivocally confirm compound identities and to quantify.   The combination of accurate mass (< 2 ppm mass accuracy), high resolution (>12,000 at *m/z* 200), and a large linear dynamic range allowed excellent quantification of typical pollutants found in these complex matricies. Accurate determination of method detection limits, limits of quantitation, and mass accuracy will require more extensive studies using matrix spiked standards. The use of MS/MS to further improve detection limits and reduce interferences will also be studied.

References
(1) "Basic Information about Benzo(a)pyrene in Drinking Water"; U.S. EPA
http://water.epa.gov/drink/contaminants/basicinformation/benzo-a-pyrene.cfm