GC-HRMS analysis for old and new POPs with GC-Tof/MS techniques

Takumi Takasuga

Shimadzu Techno Research,
Ehime University, Japan
Email: t_takasuga00@shimadzu-techno.co.jp

Biographical notes: Takumi Takasuga graduated from Ehime University, Department of Environmental Chemistry, Graduate School of Agriculture in 1985. He received his PhD in Analytical Chemistry from the Department of Applied Biological Chemistry, Graduate School of Agricultural and Life Sciences, the University of Tokyo in 2001. He is a member of Committee of Quality Control in Environmental Analysis of Dioxin (MOEJ), member of the JIS Committee in Dioxins Analysis (METI) and Vice-Chairman of Japan Society for Environmental Chemistry (JEC). He received the 2nd Technique Prize (1993) and the 5th Academy Prize for Environmental Chemistry (1996) from JEC. He gained an honorary Doctor degree from Örebro University, Sweden in 2003. He has been a Visiting Professor of Center for Marine Environmental Studies (CMES), Ehime University, Japan since 2006.

1 Introduction

Our research is focused on analytical chemistry, applied for the development or improvement of tracing methods, specifically for ultra-trace organic compounds in the environment at large and in biological samples in particular.

Since 2002 we have reported on the development of a comprehensive analytical methodology for monitoring POPs, present in environmental samples with HRMS (EI/NCI) as main method of analysis. The analytical methods for the monitoring of POPs (including newly added POPs chemicals) in the atmospheric environment were established and evaluated. The POPs monitoring results arising from frequent monitoring in ambient air at the southern super-site Japan are reported on.

In addition, the various applications of GC-HR-Tof-MS for environmental analysis were investigated. Particularly HR-Tof-MS was successfully applied, attaining such high sensitivity as sub-picogram, with high resolution full-scan information and confidently exact mass measurement within around 5 ppm. Semi-quantified data for POPs analysis were obtained by means of the isotope dilution method with GC-HR-Tof-MS and also evaluated for a comparison with the results from conventional GC-HRMS SIM data in biological samples. Additionally, it is possible to investigate and identify unknown compounds, such as those compounds interfering in routine dioxin analysis or other organohalogen compounds occurring in marine mammals.

Soils from two highly PCDD/PCDF contaminated sites with pollution from former chlor-alkali electrolysis processes using graphite electrodes (Tokyo/Japan and Rheinfelden/Germany) were screened with GC-HR-Tof-MS to detect halogenated

aromatic pollutants. At all three sites the full range of Stockholm Convention UPOPs were present at high ppb levels (and at hot spot areas TEQ-levels up to several 100,000 ng/kg soil at each site). Additionally, a wide range of polychlorinated PAHs were detected at even higher levels than PCDF. Furthermore, polychlorinated alkyl-PCDF and polychlorinated carbazoles were detected. These complex POPs mixtures were present at all these sites, suggesting that a comprehensive toxicity evaluation and risk assessment would be warranted for these and similar contaminated sites from chlorine electrolysis industry.

The GC-HR-Tof-MS method thus demonstrated its usefulness as a powerful tool for screening complex contaminated environmental matrices, including the assignment of contaminants from their accurate masses. As such, the GC-HR-Tof-MS opens a new pathway and dimension for extended fingerprinting of UPOPs sources.

Comprehensive analytical methodology using GC/Tof-MS was also applied for the investigation of organohalogen compounds in biological samples. In blubber and liver of finless porpoise, the concentration orders of legacy POPs were:

PCBs > DDTs > chlordane compounds > HCHs > HCB
> polychlorinateddiphenyl ethers (PCDEs) > HBCD > PBDEs.

Moreover, 2,3,3',4,4',5,5'-heptachloro-1'-methyl-1,2'-bipyrrole (Q1) was successfully identified in finless porpoise samples, which is one of the natural marine halogenated products and widely distributed in the environment. Halogenated natural products such as $BrCl_6$-1'-methyl-1,2'-bipyrrole and Br_2Cl_5-1'-methyl-1,2'-bipyrrole were identified also, which both are brominated congeners of Q1.

These results suggest that GC-HR-Tof-MS is a useful technique suitable for full characterisation and profiling of chemical compounds present in a whole range of sample types and for getting data of highest reliability, in addition to other analytical qualities such as selectivity, specificity, increased sensitivity and easy and accurate data interpretation.

2 List of abbreviations used

EI/NCI	electron ionisation/negative-chemical ionisation
GC-HR-Tof-MS	gas chromatography-high resolution-time of flight-mass spectrometry
HRMS	high resolution mass spectrometry
HR-Tof-MS	High resolution-time of flight-mass spectrometry
POPs	persistent organic pollutants
UPOPs	unintentional POPs.