Rapid, Sensitive Detection of Polybrominated Diphenyl Ethers by Gas Chromatography Coupled to ICP-MS

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Introduction

ICP-MS has been shown to be a sensitive, highly selective GC detector for volatile brominated compounds including pesticides[1] and alkylbromides[2]. As a bromine-specific detector for gas chromatography, ICP-MS possesses several advantages over other halogen-specific detectors. Since it is an elemental mass spectrometer, it is absolutely selective among the halogens, suffering no interference from fluorine, chlorine or iodine. In fact the only expected interferences on bromine by GC-ICP-MS are Ar_2H created in the plasma, which can cause elevated background for ^{81}Br. This can occur when hydrogen GC carrier is used, but can be eliminated by using helium carrier. When using hydrogen carrier, the use of the other Br isotope, ^{79}Br, avoids the interference. Because of the high-power, high-temperature argon plasma, ICP-MS does not exhibit the suppression of response from co-eluting compounds typical of some other elemental detectors. For the same reason, ICP-MS can tolerate a range of GC carrier gas options and flows, greatly increasing the chromatographic flexibility. Additionally, ICP-MS is capable of compound independent calibration. This is particularly useful for the quantification of compounds for which standards are expensive or unavailable such as many PBDE congeners. Concentrations of uncalibrated congeners are based on the structure (which must be known) and bromine response factor. In this work, the suitability of GC-ICP-MS for the detection and quantification of PBDEs in standards and mixtures containing PCBs is examined. Figures of merit include detection limits and response factors for various PBDE congeners, linear range as well as chromatographic conditions and retention times.

Materials and Methods

The GC-ICP-MS system consisted of an Agilent 6890 GC and Agilent 7500a ICP-MS. The GC was fitted with a programmable cool on-column injector and three-channel optional Electronic Pressure Control module. The connection between the GC and ICP-MS was via the Agilent GC-ICP-MS interface. The GC column was a thin-film Agilent DB-5 MS (0.25mm ID x 5m x 0.25 micron). PBDE standards were obtained from AccuStandard Inc., New Haven CT. In this work, optimization of both gas chromatographic and ICP-MS conditions for the separation and detection of various PBDE congeners, including PBDE 209 (decabromo diphenyl ether) are examined. Initial

GC column selection, 5m Agilent DB-5 MS, was based on the work of Bjorklund et.al.[3], but other column lengths were examined as well. The effects on retention time and chromatographic resolution of hydrogen and helium carrier at varied flow rates are examined. While hydrogen is less expensive and offers potentially better resolution at high linear velocities (shorter run times), the use of He avoids the potential interference from Ar_2H on ^{81}Br. ICP-MS conditions including RF power, carrier gas flow, sampling depth and addition of various reagent gases that are known to affect sensitivity in other GC-ICP-MS applications were examined. The addition of carbon to the central channel of the argon plasma is known to enhance the sensitivity for some high-ionization potential elements such as arsenic and selenium (IP ~9.8eV each). Since bromine has quite high IP, (11.8 eV), the addition of carbon dioxide to the argon ICP carrier gas was evaluated for potential sensitivity enhancement. To test the ability of the GC-ICP-MS system to detect low levels of PBDEs in potentially difficult matrices, PBDEs were spiked into commercial PCB mixes and chromatographed. A mixture of Aroclor 1016 and 1260 was used at 250 ppm each.

Results

Figure 1 is an extracted ion chromatogram of a mix containing 14 PBDE congeners including PBDE 209. All congeners are well separated under the conditions used. Figure 2 displays the results of the 50 ppb PBDE spike into a PCB mixture (500 ppm total). The upper trace is the extracted ion chromatogram for ^{79}Br, the lower trace, which has been inverted for display purposes, is chlorine. There is no apparent effect on the measurement of PBDEs in the presence of a large excess of PCBs. Initial detection limits in the range of 100-200ppt (ng l^{-1}) per congener were measured, though further optimization is expected to improve this. A typical calibration curve for PBDE 183 is shown in figure 3. Calibrations are linear (r^2 = 1.000) from 10 ppb to 1 ppm. Figure 4 illustrates the mass corrected response factors for several congeners between 3-Br and 10-Br for duplicate runs. Good agreement in response factor between compounds through the earlier-eluting hepta congener demonstrates the potential applicability of compound independent calibration. However, the response falls off rapidly for the higher boiling hepta congener and deca congener. While this is likely a chromatographic problem, it is being investigated.

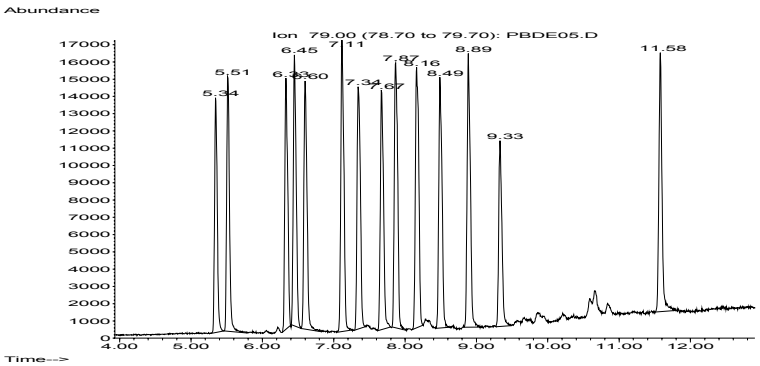

Figure 1. PBDE mix containing 14 congeners from tri-BDE to deca-BDE at 50 ppb each (tri – hepta) and 250 ppb (deca-BDE). Chromatographed on 5m DB-5MS with hydrogen carrier at 320 cm/sec

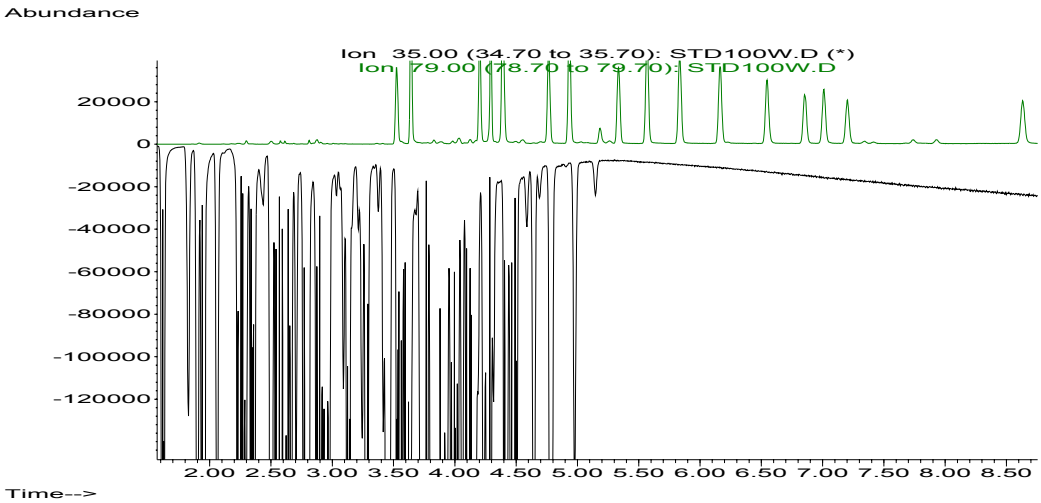

Figure 2. Mixture of 14 PBDE congeners at 50 ppb each spiked into 250 ppm each Aroclor 1016 plus Aroclor 1260. Extracted ion chromatogram for ^{79}Br on top, ^{35}Cl on bottom, inverted for ease of display.

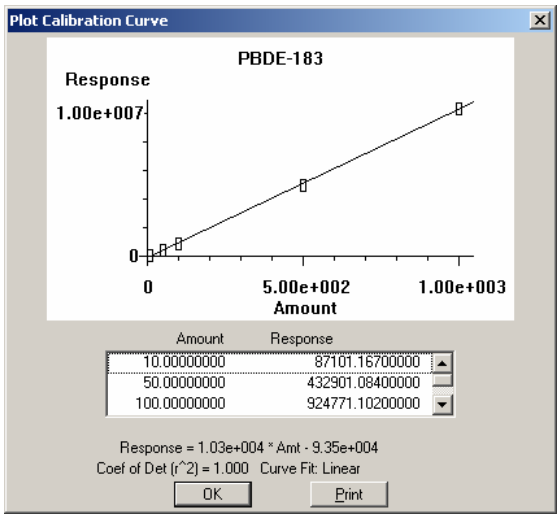

Figure 3. Typical calibration, PBDE 183, 2,2',3,4,4',5',6-hepta-BDE. 10 ppb to 1 ppm. $R^2 = 1.000$

Discussion

Preliminary results indicate that GC-ICP-MS is an excellent detector for PBDEs. The sensitivity, and bromine selectivity are likely unmatched my any other detector. Additionally, the ability of the argon plasma to tolerate either hydrogen or helium GC carrier over a wide range of flows is a significant advantage. It allows the chromatography to be tailored to the specific application rather than the constraints of the detector. Additionally, the technique, once set up, is simple to use and automate, stable and robust. Potential limitations, which have not been examined, are related to the possibility of chromatographically indistinguishable, non-PBDE, bromine containing compounds in some naturally occurring sample types. In this case, the GC-ICP-MS system would not be able to resolve these interferences from the PBDE targets. It is not known if this presents a serious limitation for some sample types and what those types may be. Possible solutions include those used with other GC detectors, including confirmation of retention time on a second column of different retention characteristics, or MS confirmation using a molecular mass spectrometer which can supply structural information. While this may seem redundant, in this case, the GC-ICP-MS would serve as a very sensitive and selective screening tool for detecting all bromine-containing

compounds in potentially very complex matrices. This would vastly simplify the task of locating and confirming the PBDE compounds by alternate MS techniques.

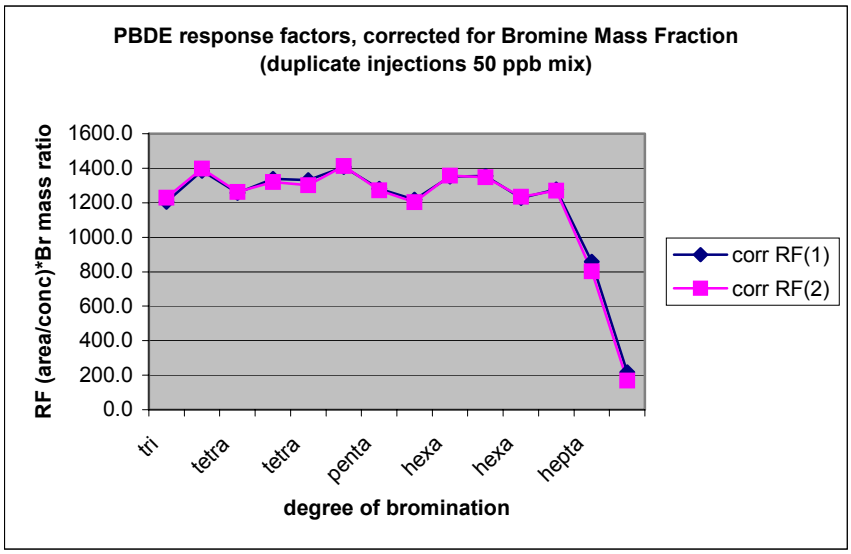

Figure 4. Compound Independent Calibration Response Factors as a function of degree of bromination.

Conclusions

While further work is likely to improve the chromatography and detection limits of PBDEs by GC-ICP-MS, the current state of the art is sufficient for most applications. Further work is needed using the technique to characterize natural samples from a variety of sources to determine its real-world usefulness. GC coupled to ICP-MS and EI or CI MS in parallel has potential to overcome the potential limitations of GC-ICP-MS alone, and could provide an alternative to GC-high-resolution mass spectrometry.

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[1] Profrock, Daniel, P. Leonhard, S. Wilbur and A. Prange, *J. Anal. At. Spectrom*., 2004, 19, 1-10

[2] Schwarz, Anastasia and K. Heumann, *Determination of Biogenic Brominated and Iodinated Volatile Hydrocarbons by GC Coupling with ECD-ICP-MS MIP-AED and MSD,* Poster Presented at 2000 Winter Conference on Plasma Spectrochemistry, Scottsdale AZ, USA

[3] Bjorklund, Jonas, P. Tollback and C. Ostman, *Evaluation of the Gas Chromatographic Column System for the Determination of Polybrominated Diphenyl Ethers,* Poster, Department of Analytical Chemistry, Stockholm University, Sweden