

DART–TOFMS: A CHALLENGING APPROACH IN RAPID MONITORING OF BROMINATED FLAME RETARDANTS IN ENVIRONMENTAL MATRICES

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Introduction

In the past few years, ambient desorption ionization mass spectrometry has become a rapidly growing technique, finding the use in many areas, including environmental analysis. Contrary to “classic” mass spectrometry, it allows the direct analysis of ordinary objects (samples) in the open atmosphere.¹ As regards ionization processes involved in this incipient technology, they can be grouped into several classes, the most common being those related to electrospray ionization (ESI) and/or atmospheric pressure chemical ionization (APCI). In any case, the way of ionization governs the nature of resulting mass spectra. In the most of applications reported until now, desorption electrospray ionization (DESI) technique has been employed.² In our study, direct analysis in real time (DART) resembling APCI has been used. Neutral metastable species are formed by electrical discharge in a gas (typically helium). Following the reaction with components of the atmosphere such as water and oxygen molecules, reactive ionic species are produced.³ In Table 1 the overview of originated ions and list of potential analytes is shown. When interfaced to a high-resolution TOFMS, identification of unknowns is possible on the basis of exact masses and accurate isotopic abundances measurement. The aim of the presented study was to explore the potential of DART–TOFMS system in a real time examination of various environmental matrices for the presence of brominated flame retardants (BFRs), and if possible, other organic contaminants. BFRs represented mainly by polybrominated biphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are persistent organic pollutants (POPs), occurrence of which in the environment is of high concern due to the various toxic effects shown for biota.

Material and methods

For DART–TOF-MS analyses, the system consisting of a DART ion source (IonSense, Danvers, Massachusetts, USA), a JEOL AccuTOF LP high-resolution TOF mass spectrometer [JEOL (Europe) SAS, Croissy sur Seine, France], and an AutoDART HTC PAL autosampler (Leap Technologies, Carrboro, North Carolina, USA) was used.

The experimental conditions were as follows: (i) DART negative-ion mode: helium flow rate: 2.9 L/min; needle voltage: 3000 V; discharge electrode: -150 V; grid electrode: -350 V; beam temperature: 350°C; for unfragmented and fragmented mass spectra acquisition, the mass spectrometer cone voltage (orifice 1) was set to -20 V and -240 V, respectively; (ii) TOFMS detection: mass range: m/z 50–1000; detector voltage: +2600 V; acquisition rate: 5 spectra/s.

Results and discussion

Gas chromatography coupled to mass spectrometry (GC–MS) operated in a negative chemical ionization mode (NCI) represents the technique most commonly used in analysis of PBDEs and other BFRs.⁴ Bromine ions are typically the base peaks in NCI mass spectra of these compounds. In spite of the relatively low masses of [⁷⁹Br]⁻ and [⁸¹Br]⁻, their selectivity is theoretically high since only a limited number of components potentially present in environmental samples are prone to yield ions capable of efficient electron capture in NCI. Thus, bromine ions are especially suitable for MS quantification purposes.⁵ Conventional BFRs analysis of real life samples typically involves purification and/or fractionation of crude extract followed by GC separation of sample components.⁶ An example of GC–MS (NCI) analysis of in-door dust containing relatively high levels of PBDE 209 is shown in Figure 1. More than 90 min are needed to prepare the sample extract for analysis and to obtain such chromatogram. In addition to the time demands, another limitation of this approach is that only bromine-containing compounds can be determined by GC–MS when employing NCI. In practice, rapid examination of samples for the content of organic bromine might be a sufficient information to recognize a contamination problem. Supposing some similarity of BFRs fragmentation under NCI conditions in GC–MS and negative APCI, as well as with regards to other facts mentioned above, the use of DART–TOFMS was considered to

represent a challenging approach enabling not only significant increase of laboratory throughput but also comprehensive sample profiling.

In the first phase of our experiments, the possibility of PBDEs ionization by DART was investigated. It should be noted that most of studies concerned with LC–MS analysis of these POPs employed atmospheric pressure photoionization (APPI).⁷ One of few studies in which negative APCI was used, documented fragmentation of nonabrominated BDE yielding (i) phenolate anions resulting from the cleavage of an ether bridge and (ii) anions resulting from bromine abstraction $[M-Br]^-$.⁸ As shown in Figure 2-A, similar results were obtained when standard solution of decabrominated BDE was analyzed by DART–TOFMS at a low voltage of cone (orifice 1) setting. Decreasing this value from -20 V to -140 V resulted in disappearance of the polybrominated anions; the only ions in mass spectrum were intensive ions $[^{79}Br]^-$ and $[^{81}Br]^-$ (Figure 2-B). While it was not possible to detect PBDEs in dust extract [previously examined by GC–MS (NICI), Figure 1] due to high chemical noise, both bromine isotopic ions were distinctly recognized in low m/z region (Figure 3-A). To remove interfering ion with a mass close to $[^{79}Br]^-$, an attempt to induce its fragmentation was undertaken. As shown in Figure 3-B this was achieved by further decrease cone voltage (-240 V).

Although very preliminary, these results indicate the potential to introduce new concepts into rapid environmental screening by employing DART–TOFMS, which minimizes sample handling and omits chromatographic separation. In addition to BFRs the information provided by both negative and positive spectra should be exploited. Of course, much more follow up research is needed with a special focus on quantification of target compounds and identification of unknowns.

Acknowledgments

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References

- Venter A., Nefliu M. and Cooks R. G. *TrAC-Trend Anal Chem* 2008; 27; 284.
- Takats Z., Wiseman J. M., Gologan B. and Cooks R. G. *Science* 2004; 306; 471.
- Cody R.B., Laramée J.A. and Durst H.D. *Anal Chem* 2005; 77; 2297.
- Cajka T., Hajslova J., Mastovska K.: Mass spectrometry and hyphenated instruments in food analysis. In: *Handbook of Food Analysis Instruments*. S. Otiles (ed.), CRC Press, Taylor & Francis Group (in press).
- Cajka T., Hajslova J., Kazda R., Poustka J. *J Sep Sci* 2005; 28; 601.
- Covaci A, Voorspoels S, Ramos L., Neels H., Blust R. *J Chromatogr A* 2007; 1153; 145.
- Debrauwer L, Riu A., Jouahri M., Rathahao E., Jouanin I., Antignac J.-P., Cariou R., Bizec B. L. and Zalko D. *J Chromatogr A* 2005; 1082; 98.
- Schlummer M., Brandl F. and Mäurer A. *Organohalogen Compd* 2004; 66; 287.

Table 1: Analytes ionized in positive and negative ion mode

Negative	Conceivable analytes	Positive	Conceivable analytes
Direct (M^+)	Ionic compounds, some electrophiles	Direct (M^+ , M^{*+})	Ionic compounds, low-IP organics
Proton abstraction $[M-H]^-$	Acidic compounds, nitroaromatics	Proton transfer $[M+H]^+$	Bases, alkenes, small alcohols, ethers, ketones, aldehydes
Adduct formation $[M+X]^-$	Unstable nitro compounds, some halocarbons	Other adducts $[M+Z]^+$	H/D exchange Polar compounds, ethers, ketones, acids, peroxides

Figure 1: GC-MS (NICI) chromatogram (m/z 79) of indoor dust

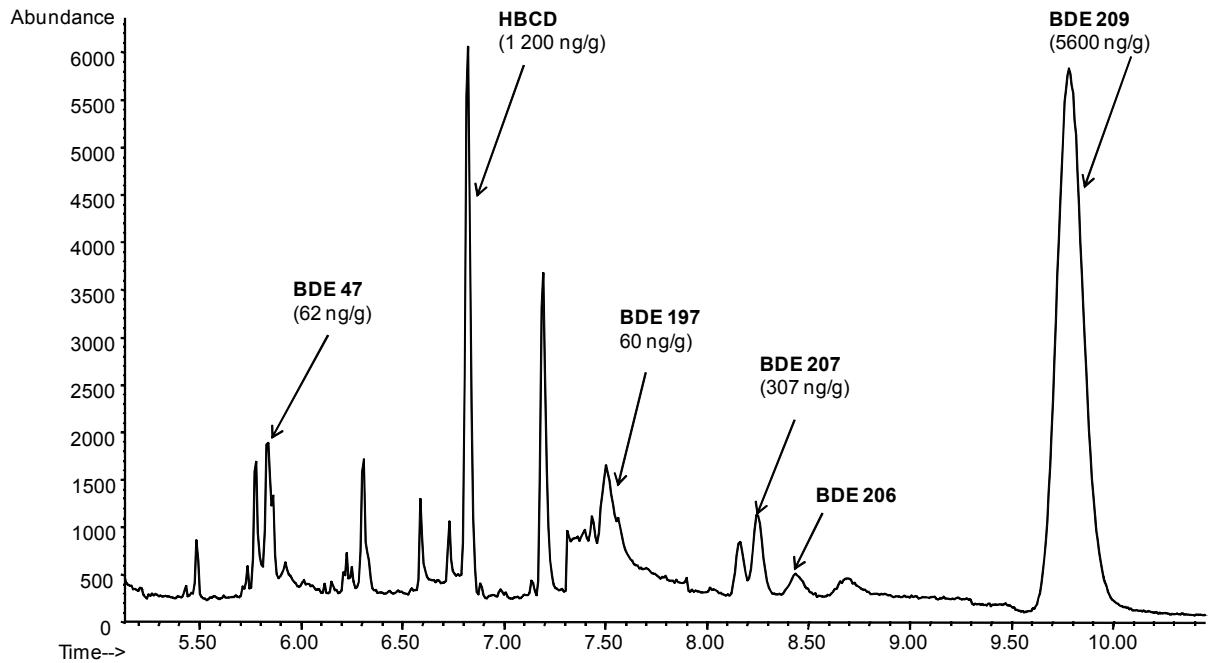
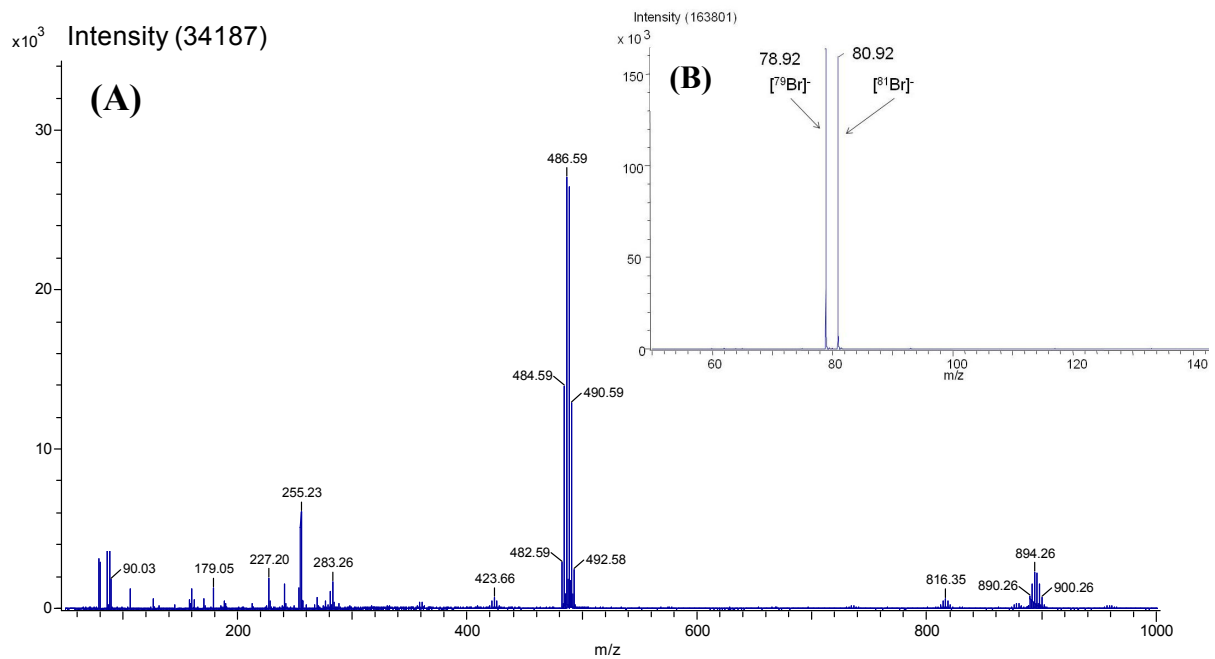
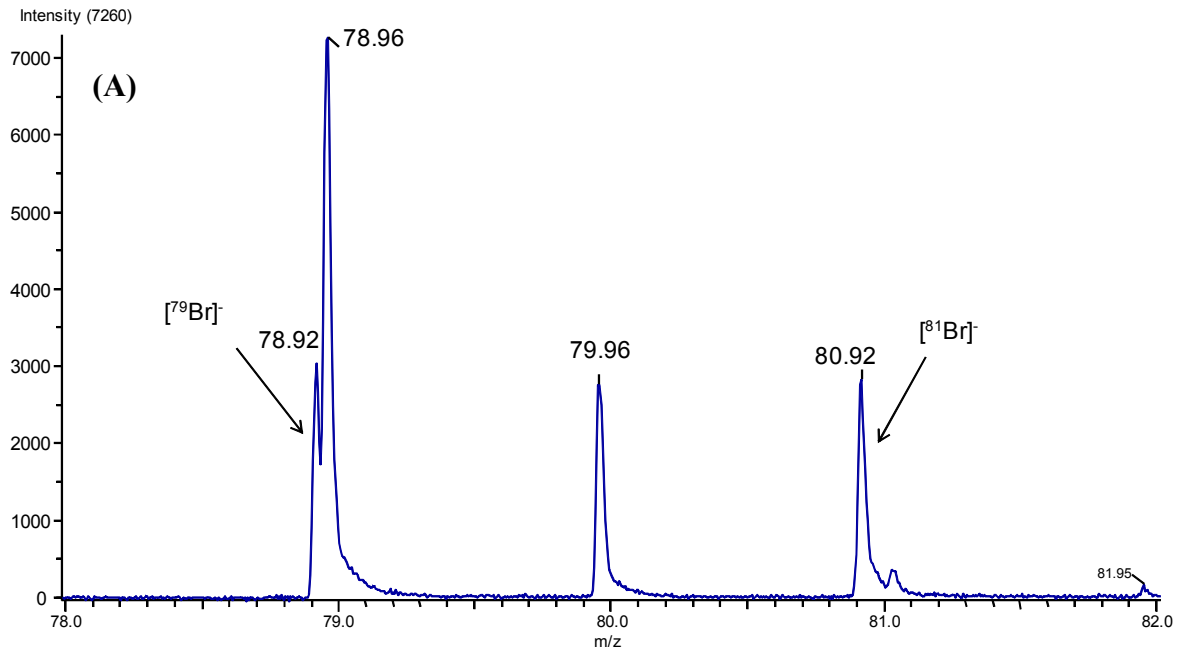


Figure 2: DART-TOFMS spectrum of standard solution of BDE 209 at a concentration of 50 $\mu\text{g/ml}$ in isooctane

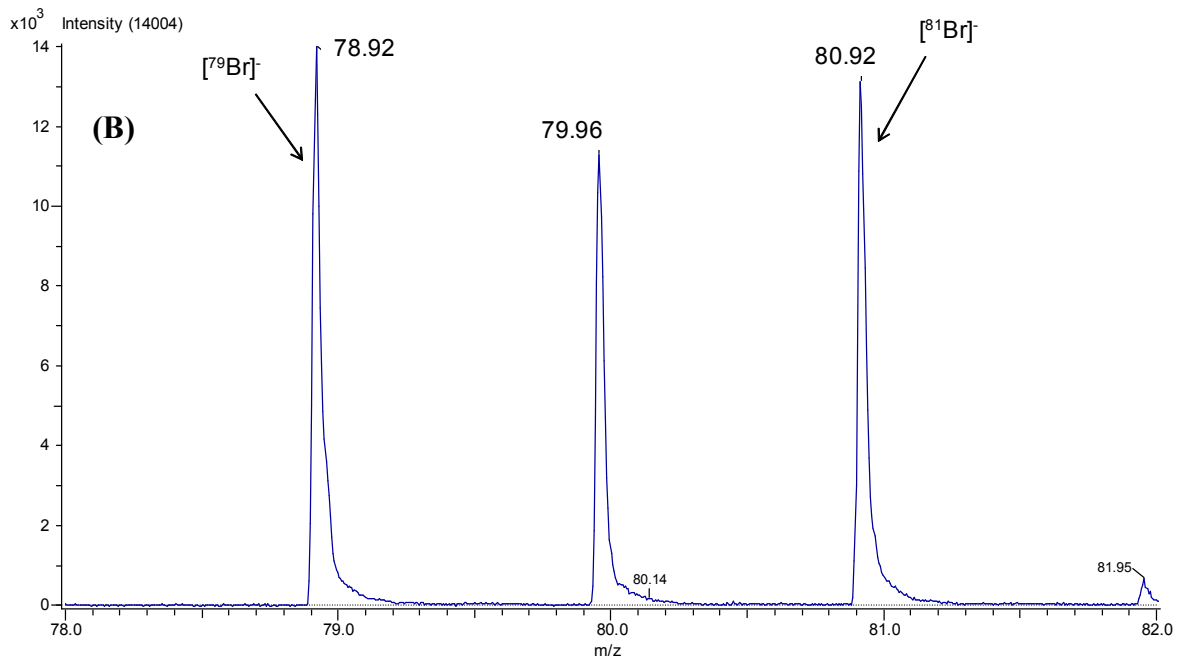


(A) ion temperature: 300°C, peaks voltage: 600 V, orifice 1: -20 V
(B) ion temperature: 350°C; peaks voltage: 400 V, orifice 1: -140 V

Figure 3: DART-TOFMS spectrum of indoor dust



(A) ion temperature: 350°C, peaks voltage: 400 V, orifice 1: -140 V



(B) ion temperature: 350°C; peaks voltage: 400 V, orifice 1: -240 V