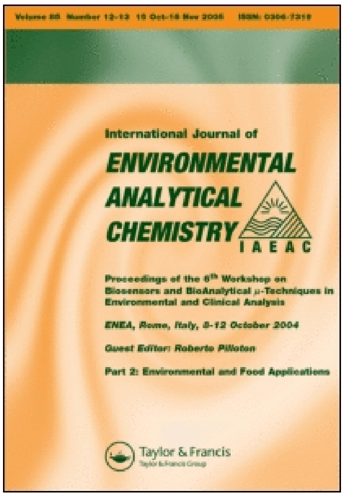

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Selective detection of unknown organic bromine compounds and quantification potentiality by negative-ion electrospray ionization mass spectrometry with induced in-source fragmentation

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Selective detection of unknown organic bromine compounds and quantification potentiality by negative-ion electrospray ionization mass spectrometry with induced in-source fragmentation

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For the detection of unknown organic bromine compounds, a liquid chromatography–mass spectrometry (LC-MS) method with negative-ion electrospray ionization (NI-ESI) and induced in-source fragmentation (IISF) was established. After LC separation, the molecules are fragmentized in the source, and bromide is detected via m/z 79 and m/z 81 based on the isotopic occurrence of bromine. In this way, the retention times of the unknown organobromine compounds are determined, and this can be used to extract additional structural information (number of bound bromine atoms, molecular mass and fragmentation scheme) from measurements in the commonly used but less sensitive scan mode. The analysis of known organobromine compounds shows that LC/NI-ESI-IISF mass spectrometry with detection of m/z 79 and 81 is more sensitive than the detection of daughter ions (LC/ESI/MS-MS). Therefore, we present a method not only for the detection of unknown organic bromine compounds, but also for the selective and sensitive detection and quantification of known organobromine compounds.

Keywords: AOBr; Bromine; Halogenated organic compounds; LC/MS; In-source fragmentation; Element-specific detection

1. Introduction

From the environmental point of view, organic halogen compounds are of special interest because they are in general characterized as toxic, persistent, and/or carcinogenic, and are very often considered as anthropogenic pollutants. Newer studies have shown that organic halogen compounds can also be produced by nature. The natural production of halogenated organic compounds is used by marine and terrestrial organisms in chemical defence and as, irritants, pesticides, or food gathering [1].

Our institute reported for the first time the occurrence of natural organic bromine compounds in freshwater [2, 3]. By differentiation of group parameter AOX into

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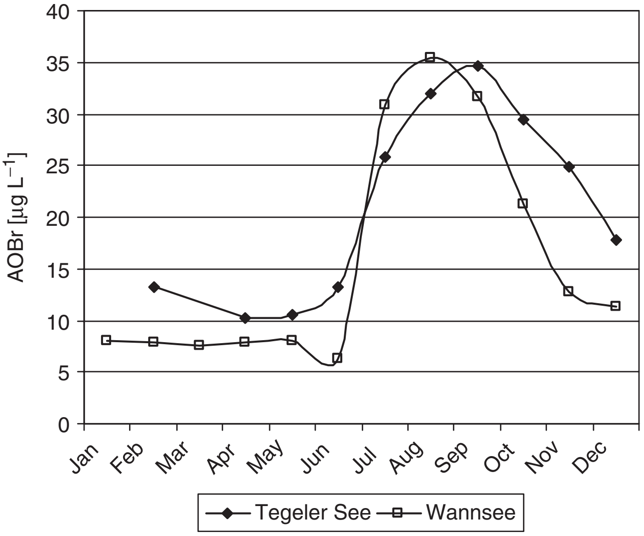

Figure 1. Annual AOBr profile of two surface waters in Berlin; Tegeler See data from [4] and Wannsee data from [5].

adsorbable organic chlorine (AOCl), bromine (AOBr), and iodine (AOI) using ion chromatography [4], it was recognized that surface waters in Berlin are characterized by an annual AOBr profile [5, 6] with elevated AOBr concentrations (up to 35 µg L^{-1}) in late summer, whereas just 10 µg L^{-1} is detectable during other months (figure 1). Such annual profiles have been observed over several years (1998–2004). It could be shown that the AOBr is autochthonous and that the formation is connected with the algae bloom in late summer [7, 8]. An enzymatic formation via bromoperoxidase is discussed in a previous publication [9].

Besides detection of the group parameter AOBr, we are interested in which compounds are responsible for the AOBr. For this reason, the AOBr was characterized based on physical and chemical properties in this study. For the detection of unknown organic compounds characterized by a hetero-atom, the selective detection of the hetero-atom by liquid chromatography/inductively coupled plasma/atomic emission spectrometry (LC/ICP/AES), liquid chromatography/inductively coupled plasma/mass spectrometry (LC/ICP/MS), or liquid chromatography/inductively coupled plasma/time-of-flight mass spectrometry (LC/ICP/TOF-MS) is the method of choice [10–12]. Element-specific detection determines the retention time of the organic compounds of interest, but structural information can only be obtained by different techniques, which do not destroy the molecules, like liquid chromatography/electrospray ionization/tandem mass spectrometry (LC/ESI/MS-MS) or liquid chromatography/nuclear magnetic resonance (LC/NMR). Very often, LC/ICP/MS and LC/ESI/MS are not available in one laboratory. Thus, we aimed to determine whether bromine-specific detection is possible by liquid chromatography/negative-ion electrospray ionization/mass spectrometry (LC/NI-ESI/MS) with induced in-source fragmentation (IISF) and detection of *m*/*z* 79 and 81 for bromide, in analogy to a published method for the detection of iodinated organic compounds [13]. The sensitivity of the liquid chromatography/negative-ion induced electrospray ionization/in-source fragmentation/mass spectrometry (LC/NI-ESI-IISF/MS) method was compared with that of LC/NI-ESI/MS-MS by analysing known brominated organic compounds. We also wanted to determine whether preliminary structural information can be obtained by conventional LC/ESI/MS, even in cases of low concentrations of unknown brominated compounds, after their retention times are known.

2. Experimental

2.1 *Standards/chemicals*

Bromochloroacetic acid, 2,3-dibromopropionic acid, 2,4-dibromophenol, and 2,4,6-tribromophenol were purchased from Dr Ehrenstorfer (Augsburg, Germany) and bromophenylacetic acid from Merck (Darmstadt, Germany). All other compounds were purchased from Sigma–Aldrich. The methanol used was gradient-grade (Baker). Ultra-pure water was produced from deionized water by treatment in an ELGA purification system (Ubstadt-Weiher, Germany).

2.2 *Solid-phase extraction*

For solid-phase extraction (SPE), different materials were tested with adequate conditioning and elution procedures for each medium. Disposable 6-mL LiChrolute® RP-C18 cartridges (500 mg; Merck, Darmstadt, Germany) were conditioned with 10 mL of ultra-pure (u.p.) water, 10 mL of methanol, and 8 mL of u.p. water, pH 5. Disposable 6-mL LiChrolut® EN (500 mg; Merck, Darmstadt, Germany), Isolut® EnV+ (500 mg; IST, Hengoed, UK) and Oasis® HLB (500 mg; Waters, Milford, MA) cartridges were conditioned with 10 mL of u.p. water, 10 mL of methanol, and 8 mL of u.p. water, pH 2. BondElut® SCX and SAX 3 mL cartridges (1000 mg; Varian, Darmstadt, Germany) were conditioned with 6 mL of u.p. water, 6 mL of methanol, and 10 mL of u.p. water, pH 2, for SCX pH 9 for SAX. The sample volume extracted was 200 mL for LiChrolute® RP-C18 at pH 5 and 100 mL for all others with a sample pH of 2, except for BondElut® SAX with pH 9. The extraction flow was 2 mL min^{-1}. After drying the cartridges with nitrogen, the RP-C18, EN, EnV+, and HLB cartridges were eluted with 15 mL of methanol (2 mL min^{-1}). The SCX cartridges were eluted with 9 mL of 1% NH_4OH in methanol and the SAX with 9 mL of 1 N HCl in methanol with a flow of 2 mL min^{-1}. The last traces of eluting solvent were purged with nitrogen gas.

2.3 *Adsorbable organic bromine compounds (AOBr)*

For the determination of adsorbable organic bromine (AOBr), the filtered (0.45 μm) and acidified water sample (conc. HNO_3, pH 2) was enriched on activated carbon. The POBr was not determined prior to enrichment, because in surface water, POBr concentrations are expected to be negligible. After combustion of the loaded activated carbon and trapping the combustion gas in deionized water with a trace of sodium sulfide, the halides were analysed by ion chromatography [4]. Ion chromatography was carried out with an IonPac AS9-SC column with AG9-SC pre-column on a

Dionex DX 100 workstation. As eluent, $NaHCO_3/Na_2CO_3/H_3BO_3$ (0.75 mM/2.2 mM/3.75 mM) with a flow rate of $2\,mL\,min^{-1}$ was used. Bromide was detected by UV absorption at 210 nm.

2.4 *Sample treatment*

For the selective detection of unknown organic bromine compounds in surface water, a surface water sample was cultivated in a batch test at 25°C to simulate an AOBr production [2, 8]. The AOBr-rich sample ($103\,\mu g\,L^{-1}$) was filtered through 0.45 µm membrane filters. For cation exchange, a 1-mL On Guard® II Na cartridge (Dionex) was rinsed with 2 mL of u.p. water and 3 mL of sample. Thereafter, 50 mL of the sample was pumped at a flow rate of $1\,mL\,min^{-1}$ through the cartridge and collected in a graduated cylinder measuring the extracted sample volume. The sample after cation exchange was concentrated 200 times with a SpeedVac concentrator (Savant, Thermo) at low pressure, with rotation, and at a temperature of 70°C.

2.5 *Liquid chromatography*

For liquid chromatography, an Agilent system (Hewlett-Packard Series 1100, Waldbronn, Germany) was used, comprising a vacuum solvent degassing unit, a binary high-pressure gradient pump and an automatic sample injector. The separation was performed on a phenyl-hexyl column (Phenomenex®: Luna 3 µm; 150 × 2 mm). A linear gradient with a flow rate of $0.20\,mL\,min^{-1}$ was used. The solvents were A 80% u.p. water with 20% methanol and B 5% u.p. water with 95% methanol. The linear gradient elution programme was as follows: from 10% B to 40% B in 10 min, holding 40% B for 20 min, raising the amount of B to 60% in 10 min, to 100% B in 5 min and reducing it to 10% B in 10 min which was then held for 10 min. The column oven was set to 35°C, and the injection volume was 10 µL.

2.6 *Mass spectrometry (MS)*

The LC was coupled with an orthogonal Z-spray-electrospray interface to a mass spectrometer (Quattro-LC; Micromass, Manchester, UK). Nitrogen generated from pressurized air (Whatman, Haverhill, MA) was used as drying gas ($900\,L\,h^{-1}$) and nebulizing gas ($85\,L\,h^{-1}$). The desolvation temperature was 280°C, and the source temperature 120°C. NI-ESI was used for the detection of bromide. The capillary voltage was 3.4 kV, and the skimmer voltage was 1.5 V. The cone voltage was 100 V for IISF. The first quadrupole was used in the single ion monitoring (SIM) mode and was set to m/z 79 and 81. For the detection of organic bromine compounds, a cone voltage of 26 V was used. All other parameters were as described above. The compounds were detected in the scan mode, recording all m/z values in the range of 150–600, respectively, and m/z 350–800 in a second analysis. Known organic bromine compounds were detected in the multi-reaction-monitoring (MRM) mode. Argon 5.0 (Messer, Griesheim, Germany) was used as collision gas. The pressure in the collision cell was 1.3×10^{-3} mbar. The collision energies and the product ions were determined by infusion experiments (table 1).

3. Results

Characterizing the AOBr by its volatility and polarity is necessary for an estimation of the usefulness of liquid (LC) or gas chromatography (GC). Sparging experiments with nitrogen revealed that the AOBr is not volatile. This was important because samples used for AOBr were not sparged before analysis (see section 2). Equal AOBr values were determined in an original lake water sample (AOBr = 21.9 $\mu g\,L^{-1}$) and in an aliquot which was vented with nitrogen for 1 h. SPE was carried out with a surface water sample cultivated in a batch test using different stationary phases (figure 2). The AOBr was determined in the water sample before and after extraction as well as in the extract. At pH 5 with LiChrolute® RP-C18, more than 90% of the AOBr is not extractable, and just 4% of the AOBr is determined in the extract, which provides the first evidence for polar properties of the AOBr. After extracting samples acidified to pH 2 with LiChrolute® EN, Isolute® EnV+ and Oasis® HLB, only 18, 15, and 42% of the initial AOBr was found in the extracted water sample. Although most of the AOBr is extractable, just 45, 29, and 49% of the original AOBr were found in the extract. It is supposed that the missing amount remains on the SPE material and cannot be eluted. The best extraction and elution rate was achieved with the anion exchange cartridge BondElut® SAX (83% at pH 9), indicating anionic properties of most of the AOBr. The SPE methods were not optimized further, because they were just used to

Table 1. Molecular weight, retention time, daughter ions, and collision energies used for LC/NI-ESI/MS-MS.

Compound	Molecular mass	Time window (min)	Daughter ions	Collision energy (V)
Bromochloroacetic acid	173	0–9	129	15
2,3-Dibromopropionic acid	231	9–15	80	6
Bromophenylacetic acid	105	15–30	61	9
2,4-Dibromophenol	251	30–45	80	20
2,4,6-Tribromophenol	331	45–55	331[a]	15

[a] Detection without fragmentation.

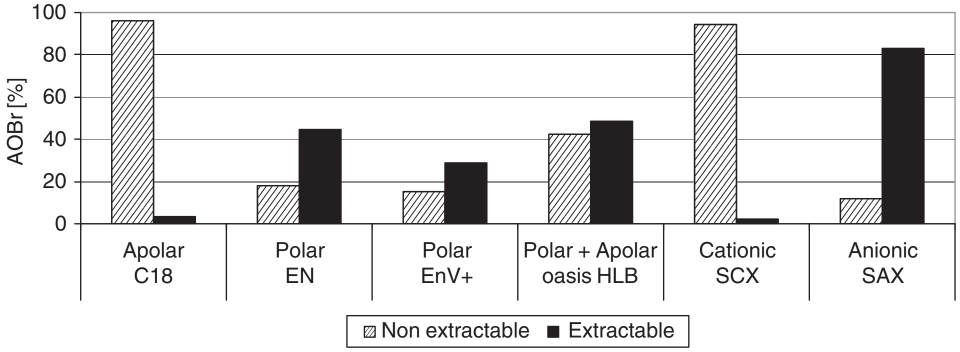

Figure 2. AOBr distribution of AOBr-rich surface water samples after solid-phase extraction.

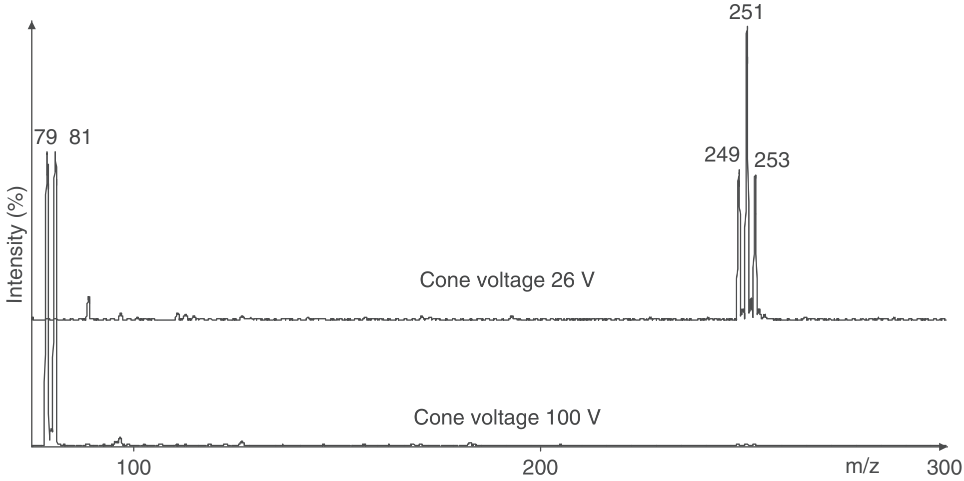

Figure 3. Mass spectra of 2,4-dibromophenol determined by infusion and NI-ESI/MS at different cone voltages.

characterize the AOBr. Both non-volatility and polar/anionic properties require separation by LC.

The detection of unknown organic compounds can be simplified if the compound of interest is characterized by a functional group or a hetero-atom. Putschew *et al.* [13] showed that iodinated organic compounds can be traced via iodide by mass spectrometry after LC negative-ion electrospray ionization (LC/NI-ESI) if an induced in-source fragmentation (IISF) is used. The iodinated organic compounds are already destroyed in the source of the MS, and *m*/*z* 127 is detected. It is expected that the LC/NI-ESI-IISF/MS method is also suitable for the selective detection of brominated organic compounds. The NI-ESI mode has to be used, even in the case of the brominated organic compounds because the expected fragment produced is bromide, which has a negative charge and can only be detected if NI-ESI is applied. Due to the much lower mass of bromine compared with iodine, it is necessary to check if the *m*/*z* 79 and 81 is selective for bromine/bromide and if the natural occurrence of the two bromine isotopes can be used to enhance the selectivity. *m*/*z* values lower than 100 are often detected by LC/ESI/MS and can originate from the eluent used or from other non-brominated compounds. At the beginning, infusion experiments were performed with several different brominated organic compounds for the evaluation of the appropriate cone voltage to fragmentize all compounds selected. In figure 3, the mass spectra of 2,4-dibromophenol analysed with two different cone voltages are displayed. A moderate cone voltage of 26 V leads to the detection of the molecular ion with its characteristic isotopic pattern for two bromine atoms. By applying a high cone voltage of 100 V, the molecular ion is not detectable, and both bromide isotopes *m*/*z* 79 and 81 are visible. For the IISF, a cone voltage of 100 V is necessary to produce bromide as a fragment. Bromine appears in nature as ^{79}Br and ^{81}Br with a ratio of one. The isotopes and the isotopic ratio can be used as qualification criteria to enhance the selectivity. Organic bromine compounds are definitely detected if the signal of *m*/*z* 79 and 81 has the same intensity and additionally if LC is applied the same retention time.

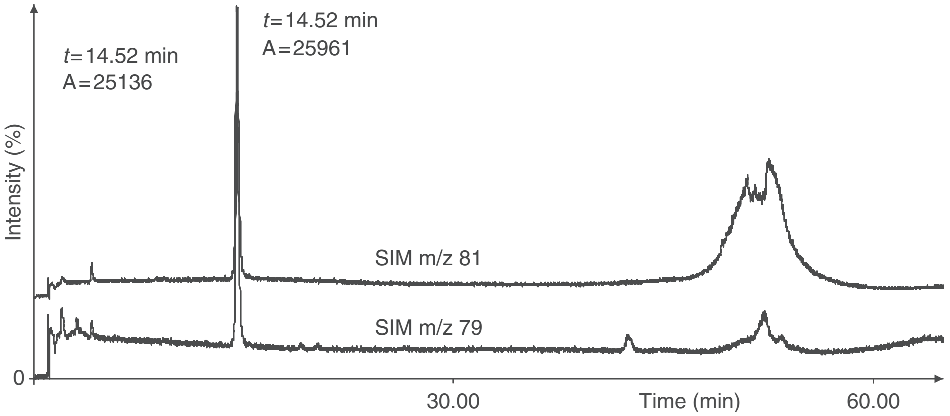

Figure 4. Chromatogram (TIC) of 2,3-dibromopropionic acid measured by LC/NI-ESI-IISF/MS and detection of *m/z* 79 and 81 in the SIM mode.

Figure 4 shows the SIM traces *m/z* 79 and 81 for 2,3-dibromopropionic acid after LC separation. The retention time of the signal in traces *m/z* 79 and 81 are equal as well as the responses (area), and thus the criteria for selective detection of brominated organic compounds via bromide after LC separation are fulfilled.

For the selective detection of unknown organic bromine compounds in surface waters, a sample with an AOBr of 103 μg L^{-1} was concentrated after cation exchange to prevent precipitation. The sample was analysed by LC/NI-ESI-IISF/MS, and *m/z* 79 and 81 were recorded in the SIM mode. Several peaks are visible in the two traces (figure 5a). Eight of these (marked by an arrow) fulfil the criteria that the signal intensities in both traces are the same. Additionally, the same sample was analysed by the common LC/NI-ESI/MS in scan mode, using a moderate cone voltage of 26 V (figure 5b). The NI-ESI mode was used because SPE showed that most of the AOBr is anionic. The analysis in the scan mode was performed for two different *m/z* ranges: 150–600 and 350–800. It should be mentioned that the use of a smaller *m/z* range can raise the sensitivity. Based on the retention times determined by the selective detected organic bound bromine, it is possible to extract molecular ions from the scan chromatogram, which is generally a less sensitive detection mode. As an example, the organic compound with a retention time of 6.25 min was selected for the extraction of the mass spectrum (figure 5c). Several *m/z* values differing by 2 mass units, as expected for brominated compounds, are detected. Furthermore, the detected *m/z* values differing by two mass units have the same intensity, and thus one bromine atom is bound in the molecule. For this compound and several more for this water sample, information about the molecular weight, possible fragmentation pattern, and number of bound halogen atoms can be obtained. Table 2 gives an overview of all brominated compounds detected in the analysed surface water sample. The retention times, peak areas, and ratio of the areas are given. The ratio of *m/z* 79 to 81 is always close to one and proves the bromide identity. The molecular ions as well as the number of the halogens bound are given, too. Thus, it is possible to detect unknown organic bromine compounds by LC/NI-ESI-IISF/MS, as confirmed by the isotopic pattern of the molecular ions obtained after LC/NI-ESI/MS in the scan mode.

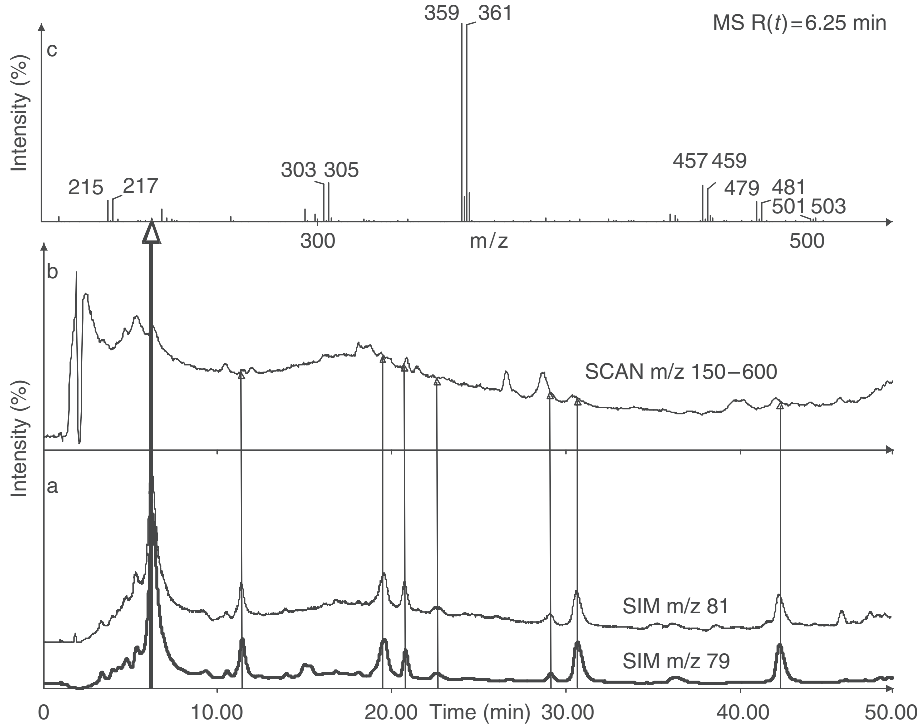

Figure 5. LC/ESI/MS analysis of a surface water sample (AOBr 103 μg L^{-1}) concentrated 200 times after Na-cation exchange. (a) *m*/*z* 79 and 81 after LC/NI-ESI-IISF/MS. (b) LC/NI-ESI/MS with detection of *m*/*z* 150–600 in the scan mode. (c) Mass spectrum at 6.35 min. Arrows indicate potential organic bromine compounds.

Table 2. Retention times, peak areas of *m*/*z* 79 and 81 of selective detected organobromine compounds (LC/NI-ESI-IISF/MS) in an AOBr-rich surface water sample and structural information evaluated from the mass spectra obtained by LC/NI-ESI/MS in the scan modes: *m*/*z* 150–600 and 350–800.

Rt (min)	*m*/*z* 79 area	*m*/*z* 81 area	*m*/*z* 79/81 area ratio	Base peak	Molecular ion (M–H)-	*n* (halogen)
6.3	638 435	612 850	1.0	359/361	742	1Br
11.5	110 792	122 597	0.9	373/375	458	1Br
19.6	161 376	159 551	1.0	323/325	443	1Br
20.9	60 479	72 546	0.8	187	387	1Br + 1Cl
22.8	23 565	30 687	0.8	257	365	1Br
28.6	21 844	28 197	0.8	337/339/341	457	1Br
30.4	169 744	166 148	1.0	395/397/399	417	1Br + 1Cl
42.0	156 131	131 088	1.2	301/303	409	1Br + 1Cl

We also investigated whether quantification of the organic bound bromine content is possible by LC/NI-ESI-IISF/MS. For this purpose, different brominated organic compounds with a concentration of 1–1000 μg L^{-1} bromine were analysed (table 3). Over that concentration range, linear calibration is possible for all compounds via *m*/*z* 79 and 81 with correlation coefficients better than 0.98, whereby a quantification using

Table 3. Linear calibration of different organobromine standards measured by LC/NI-ESI-IISF/MS for *m*/*z* 79 and 81.

Compound	*n* (bromine)	Calibration of *n* (bromine)		
		Slope	*y*-intercept	R^2
m/*z* 79				
Bromochloroacetic acid	1	478	2840	0.9867
Bromophenylacetic acid	1	67	94	0.9978
2,3-Dibromopropionic acid	2	235	629	0.9986
2,4-Dibromophenol	2	103	1	0.9986
2,4,6-Tribromophenol	3	456	1721	0.9939
m/*z* 81				
Bromochloroacetic acid	1	603	965	0.9997
Bromophenylacetic acid	1	64	578	0.9995
2,3-Dibromopropionic acid	2	299	424	0.9998
2,4-Dibromophenol	2	117	237	0.9999
2,4,6-Tribromophenol	3	408	3251	0.9997

Table 4. Response (area) and signal/noise ratio for five organobromine compounds ($c = 1000\,\mu\mathrm{g\,L^{-1}}$ bound bromine) measured by LC/NI-ESI-IISF/MS and LC/NI-ESI/MS-MS and limit of detection ranges.

		Response (area)		Response ratio	Signal/noise ratio			
	Conc. (μg L^{-1})	MRM	IISF	IISF/MRM	MRM	IISF	LOD (MRM) (μg L^{-1})	LOD (IISF) (μg L^{-1})
Bromochloroacetic acid	2160	49 290	320 061	6	302	81992	$5 < x < 100$	<1
Bromophenylacetic acid	2660	n.d.	43 638	–	1	123	>1000	1
2,3-Dibromopropionic acid	1450	6080	167 722	28	127	730	$5 < x < 100$	5
2,4-Dibromophenol	1580	602	93 930	156	8	647	$100 < x < 1000$	5
2,4,6-Tribromophenol	1380	23 563	644 848	27	121	844	$5 < x < 100$	<1

m/*z* 81 gives more accurate results, because the correlation coefficients are always better than 0.9995, due to less interference with other fragment ions. But as can be seen by the different slopes, the signal depends on the structure, meaning that the bromine content of unknown compounds cannot be quantified.

We also compared the sensitivity of the LC/NI-ESI-IISF/MS method with the commonly used MS detection in the MRM mode using five brominated organic compounds. Table 4 lists the concentrations used, which are all equal if the concentration is related to the bromine amount, the response, as well as the signal-to-noise ratio. As can be seen from the response ratios, the LC/NI-ESI-IISF/MS technique is the most sensitive method for all five standard compounds. The signal-to-noise ratios are always much higher for the IISF measurements than for the MRM analysis, showing that the selective detection of brominated organic compounds is more sensitive than MRM. It is also obvious that the sensitivity varies for the different standards and different MS techniques, which shows the structural dependency for both detection methods. Detection limits (LOD) and limits of quantification were not determined. In the MRM mode, only three standard concentrations of 1000, 100, and 5 μg L^{-1} bromine were measured. Therefore, only LOD ranges are given in table 4.

4. Conclusions

NI-ESI/MS with IISF is a selective detection method for unknown organic bromine compounds. The selective detection was confirmed by the response ratios of the two bromide isotopes close to one, identical retention times for the two bromine isotopes after liquid chromatography, and the detection of bromine compounds at identical retention times in the scan mode with the characteristic isotopic pattern of bromine. A prerequisite for the selective bromine detection by LC/NI-ESI-IISF/MS is the easy loss of bromide during in-source fragmentation. The application of LC/NI-ESI-IISF/MS is additionally a sensitive tool for the detection of known bromine compounds. For example, 2,3-dibromopropionic acid can be detected with a 30-fold higher sensitivity than in the highly selective and sensitive MRM mode. The application of IISF/MS is a tool for those who do not have the facilities to perform an LC/ICP/MS analysis to trace unknown brominated organic compounds.

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