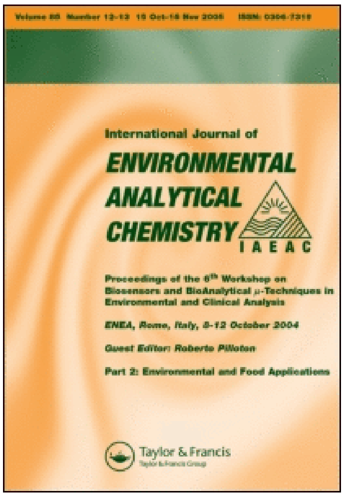

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Determination of Halide Traces in Environmental Samples by Mass Spectrometric Isotope Dilution Analysis†

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Mass spectrometric isotope dilution analysis is used for the first time to determine traces of bromide and chloride in environmental samples. This technique is an absolute method and is used especially for the standardization of other analytical processes. The principle of the isotope dilution technique is explained using Cl, Br and I. Ionization in the mass spectrometer takes place by the formation of negative halide ions on a hot rhenium filament. The examples given are the Cl^- analysis of rain and snow as well as the analysis of traces of Br^- and Cl^- in surface snow taken from varying distances away from a highway. The latter analysis is compared with results using ion selective electrodes. Unlike the concentration of Br^-, the Cl^- concentration in surface snow continually decreases, the further away the snow is from the highway. Br^- analyses of aerosol from the periphery of the town of Regensburg show that a significant portion of the aerosol bromide originates from traffic exhausts.

KEY WORDS: Chloride, bromide, mass spectrometry, isotope dilution, snow, aerosol.

INTRODUCTION

Owing to the fact that far-reaching decisions depend on analytical values in the field of environmental protection, accurate results are exceedingly important. Mass spectrometric isotope dilution analysis (MS-IDA) is an absolute method and for this reason it is particularly suitable for producing accurate analytical data.[1] Detection limits of 10^{-9} g and less

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can be achieved for certain elements by mass spectrometry hence this method is one that is preferred for trace analysis and is mainly used for calibrating other analytical techniques. Apart from the advantage of precise and accurate results, another advantage is, that there is no need for quantitative isolation of the element to be analysed after isotope dilution. This often represents a problem when the quantity of the element to be analysed is minute. In addition, due to the ionization technique in the mass spectrometer and because of the mass number of the isotopes, the technique is specific.

MS-IDA is not used as often for environmental samples as it is in other fields of analysis. Although there are some examples of determining traces of lead, cadmium and thallium in samples from the environment,[2–5] non-metals have not yet been analysed in this field by MS-IDA.

In this publication we want to explain methods of determining traces of the halides, chloride and bromide, using this technique, with the aim to check and standardize other methods of environmental analysis, MS-IDA was limited in the present investigation to samples of snow, rain and aerosol which are of common interest in environmental analysis.[6–10]

MASS SPECTROMETRIC MEASUREMENTS OF HALIDES

One ionization method in mass spectrometry is thermal surface ionization of the elements to be examined on a hot metal filament.[11] The metals are emitted as positive ions from the hot surface of the metal filament.[12] If elements with great electron affinity are being examined, e.g. halogens, the emission of negative ions is possible and this permits the analysis of these non-metals by thermal ionization. Shields *et al.*[13] and Heumann *et al.*[14] used the formation of negative ions of chlorine for exact determination of isotope ratios which is an important pre-requisite of MS-IDA. Catanzaro *et al.*[15] and Heumann *et al.*[16] used this formation for isotope ratio measurements of bromine. It has been shown in the meantime that the formation of negative ions in the mass spectrometer can also be used for iodine analysis.[16]

The ion yield β of negative ions which are emitted from a hot metal filament can be described by Eq. (1):[17]

$$\beta=\frac{n_-}{n_-+n_0}=\left[1+\frac{g_0}{g_-}\cdot\exp\left(\frac{W-EA}{k\cdot T}\right)\right]^{-1} \tag{1}$$

$n_{-,0}$ number of negative ions and neutral atoms emitted from the metal surface

$g_{-,0}$ statistical factors of ion and atom

W work function of electrons (Re $= 4.7-5.1$ eV)
EA electron affinity (Cl $= 3.61$ eV, Br $= 3.36$ eV, I $= 3.06$ eV)

For the isotope ratio measurement of chlorine and bromine a single focusing mass spectrometer (Varian MAT, Type CH5-TH) with a double-filament ion source and a Faraday cup as a detector is used. The filaments consist of rhenium. The best precision of the isotope ratio measurement is achieved when a solution of $[Ag(NH_3)_2]X$ ($X^- = Cl^-, Br^-$) is deposited on the evaporation filament and dried under a heat lamp. In the ion source the temperature of the ionization filament is increased stepwise up to a temperature of 1850°C.

Using sample amounts of 1 μmol halide with natural isotope composition, ion intensities are achieved on the Faraday cup in the range of 10^{-11} to 10^{-10}A for $^{35}Cl^-$ and in the range of 10^{-11} to 5×10^{-11} for $^{79}Br^-$. In all the analyses, the isotope intensities of $^{35}Cl^-$ and $^{37}Cl^-$ or the intensities of $^{79}Br^-$ and $^{81}Br^-$ are measured 10 times in succession in cycle (1 series of measurements). From each series the mean of the isotope ratio $^{37}Cl/^{35}Cl$ or $^{81}Br/^{79}Br$ is calculated. The standard deviation of these isotope ratios in one series of measurements is $\leq 0.1\%$.

ISOTOPE DILUTION TECHNIQUE FOR HALIDE ANALYSIS

Figure 1 demonstrates the principle of MS-IDA for determining traces of chloride and bromide using chloride as an illustration. The sample to be analysed is mixed with a known quantity of spike and the spike must have a different isotope composition than the sample. The isotope used in an enriched form is usually the one which has the least natural abundance, consequently a ^{37}Cl spike is used in chloride analysis and an ^{81}Br spike in the analysis of bromide. The sample and the spike halide are well mixed together; if the sample is an aqueous solution, simple mixing is sufficient, but if it is a solid, it has to be decomposed. Part of the element which has been diluted in this way is isolated and the isotope ratio R is determined using the mass spectrometer. R of the isotope diluted sample can be expressed as follows:

$$R = \frac{N_S \times h_S^2 + N_{Sp} \times h_{Sp}^2}{N_S \times h_S^1 + N_{Sp} \times h_{Sp}^1} \tag{2}$$

If one solves the equation for N_S, one obtains:

$$N_S = \frac{N_{Sp} \times (h_{Sp}^2 - R \times h_{Sp}^1)}{R \times h_S^1 - h_S^2} \tag{3}$$

N	number of atoms
h	isotope abundance [%]
R	isotope ratio $^{37}Cl/^{35}Cl$ or $^{81}Br/^{79}Br$
Index	1 lighter isotope ^{35}Cl or ^{79}Br, 2 heavier isotope ^{37}Cl or ^{81}Br, S sample, Sp spike

There are no known isotope variations of chlorine and bromine in environmental samples and on these conditions, the natural isotope abundances h_S can be substituted in Eq. (3) ($^{35}Cl = 75.77\,\%$; $^{37}Cl = 24.23\,\%$; $^{79}Br = 50.69\,\%$; $^{81}Br = 49.31\,\%$).[18] Equations (4a) or (4b) respectively are valid for the analysed quantity X of chloride or bromide in μg:

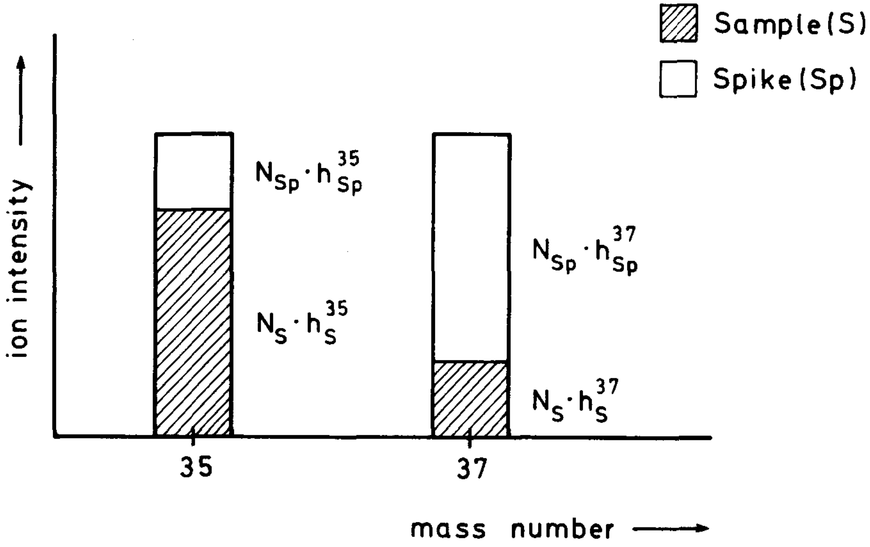

FIGURE 1 The principle of the MS-IDA of halides (example: chloride).

$$X(\mathrm{Cl}^-) = 5.887 \times 10^{-17} \times N_S \quad [\mu g] \qquad (4a)$$

$$X(\mathrm{Br}^-) = 1.327 \times 10^{-16} \times N_S \quad [\mu g] \qquad (4b)$$

In principle, iodine can also be determined by MS-IDA. However, because iodine, unlike chlorine and bromine, only has one stable isotope, one must use the radioactive long-lived ^{129}I as a spike isotope. Owing to the fact that natural iodine consists of 100% ^{127}I and on condition that the spike is also mono-isotopic, Eq. (3) simplifies itself for iodine analysis to Eq. (5):

$$N_S = N_{Sp}/R \tag{5}$$

R isotope ratio $^{129}I/^{127}I$

EXPERIMENTAL

Rain and snow samples

From January to May 1979 rain and snow were collected on the roof of the Chemistry Institute of Regensburg University on the town periphery in the following way: Four polyethylene funnels, each having a diameter of 35 cm, were connected by means of polyethylene tubes and Y-brackets with a 1 l polyethylene flask. Sample of rain and snow accumulated in the flask during a period of rain and snow. During sampling there was a more or less strong westerly wind. The average temperature and average air pressure were registered. One sample weighed between 100–250 g. Approximately 100 g of one sample was accurately weighed in a 250 ml polyethylene beaker and approximately 1 g ^{37}Cl spike solution was added to the sample. The spike solution contained 1.014×10^{19} ions Cl^- per g solution and had an isotope distribution of $^{35}Cl = 24.63\%$, $^{37}Cl = 75.37\%$. After the solutions of the spike and the sample had been stirred up and thoroughly mixed, 0.5 ml of saturated silver nitrate solution were added and left to stand for about 30 min so that the AgCl could precipitate. After this, the solution was filtered through a cellulose nitrate filter (Sartorius, Type 11301), and then to purify it, the AgCl was dissolved again in some drops of a semi-concentrated NH_3 solution. The silver chloride was then precipitated again with concentrated HNO_3. After being filtered the precipitate was dried at 60°C and kept in a non-transparent flask until mass spectrometry began. It was found advisable to reprecipitate the AgCl precipitate since impure samples produce a less exact isotope ratio measurement.[19] The AgCl had to be kept away from light until measurement because the chlorine isotope fractionates slightly when AgCl is decomposed by light of a natural wave length distribution.[20] Shortly before the mass spectrometric measurement was taken, 1 to 2 drops of a 15% NH_3 solution were added to the sample and placed on the evaporator filament of the thermal ion source of the mass spectrometer using a microliter injector. All the chemical processes were carried out in a laboratory in which nobody had worked before with chemicals to reduce the danger of contamination.

Snow samples of 100 g surface snow (down to a depth of 4 cm) were also taken from a field near the main highway leading from Regensburg to Passau. These samples came from sites 2, 10, 20, 30, 40, 50 and 300 m away from the highway. Snow had fallen three days before sampling. Salt (NaCl) has been strewn on the highway at regular intervals after the snow had fallen and before sampling. In order to determine the chloride in the snow samples using MS-IDA, we proceeded in the same way as we did with the samples of rain, except for taking snow samples at a weight of 10–30 g owing to their higher chloride content. When bromide traces were determined using MS-IDA, samples weighed between 50 and 70 g and each sample was mixed with approximately 1.8 g of an accurately weighed amount of a bromide spike solution. The spike solution contained 6.63×10^{17} Br^- ions per g spike solution and had an isotope distribution of $^{79}Br = 2.161\,\%$, $^{81}Br = 97.839\,\%$. Both the bromide and the chloride spike mentioned above had been purchased from Oak Ridge Nat. Lab. as sodium salts and the spike solution had been made by the addition of water. After the spike had been added, the sample solutions were evaporated to approximately 3 ml in a rotation evaporator. Due to the surplus Cl^- in the samples, the Br^- had to be separated by column chromatography. For this purpose the solution was placed on a column (20 cm long, 1 cm diameter) which was filled with the strongly basic exchanger AG1-X10, 200–400 mesh (Bio-Rad) and eluted with 0.4 M $NaNO_3$ solution. The bromide, which had been completely separated from the eluted chloride, was contained in the 40–60 ml elution volume. The bromide fractions were retained in a polyethylene beaker and the Br^- precipitated with a $AgNO_3$ solution. Measurements were taken using mass spectrometry as in chloride analysis. For analytical comparison, an aliquot part of each initial sample was measured using a Cl^- selective (Orion Research, Type 96–17) and a Br^- selective electrode (Type 94-35 A) and compared with a calibrated solution of known content. The bromide content of the salt used on the highway was measured using MS-IDA; the sample weights were approximately 50 mg and there was roughly 1 g of Br^- spike solution. Samples were treated in the same way as the samples of snow.

Aerosol samples

Figure 2 shows a diagram of the sampling apparatus which was used for the analysis of Cl^- and Br^- in aerosol. The air was drawn through a cellulose nitrate filter (Sartorious, Type 11301050, pore size 8 μm) of 40 mm diameter. It was then conducted through a glass bubble tube (diameter 50 cm, height 34 cm) which contained 100 ml of a 3 % super pure NaOH solution and spike solutions of approximately 4 g ^{81}Br or 1 g ^{36}Cl.

At the bottom of the bubble tube there is a frit which distributes the drawn in air in the solution in the form of small bubbles of gas. In order to prevent fine drops from spraying, a spray loop was casted onto the upper part of the bubble tube. Any drops which happened to escape were caught in a spray trap. A pump working at a maximum capacity of 2.7 m^3/h and a flowmeter completed the system. After the air had been drawn in, the solution in the bubble tube was conducted into a polyethylene beaker and both the bubble tube and the spray trap were rinsed with tetradistilled water. After this, the solutions which had been collected were acidified with HNO_3 and the silver halide was precipitated with a few drops of $AgNO_3$ solution. After the cellulose nitrate filter had been weighed, it was dissolved in a polyethylene beaker using 30 ml of a 10% super pure NaOH solution. The filter dissolves easily in the warmth. Then the sample was mixed with a spike solution of, approximately either 4 g ^{81}Br or 1 g ^{37}Cl treated in the manner described above for the solution from the bubble tube. In this way both laboratory aerosol and aerosol from outside the Chemistry Institute in Regensburg were analysed.

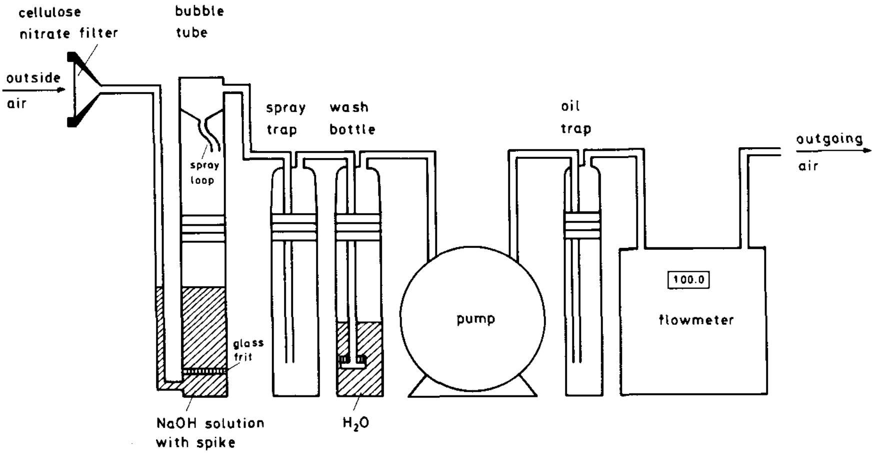

FIGURE 2 Apparatus for halide trace determination in aerosol by MS-IDA.

RESULTS AND DISCUSSION

Rain and snow

Table I shows the chloride traces determined by MS-IDA in samples of rain and snow which were taken over a period of 5 months on different days in Regensburg. Using these data, we were able to demonstrate that isotope dilution technique combined with negative thermal ionization mass spectrometry can be applied in the trace analysis of halides.

The samples of snow and rain contained between 0.3 and 2.1 μg/g chloride. These are to be understood as average values registered during one period of rain or snow according to our manner of sample collection. These trace values correspond to those obtained by examinations of rain and snow from places which are further away from the sea.[21] Compared with other places, the chloride content hardly fluctuates. A noticeable fact is that the precipitation in January and February had a relatively high chloride content, whereas the rain of a thunderstorm in May contained the least chloride. This can be accounted for by a different proportion of chloride of a maritime origin.

TABLE I

Chloride content in samples of snow and rain from Regensburg/Bavaria (1979)

Date	T [°C]	p [mbar]	Precipitation	Cl^- content [μg/g]
Jan. 27	2	954	snow and rain	2.1
28	0	951	snow	0.7
30	1	959	snow and rain	1.3
Febr. 8	1	959	snow and rain	1.3
12	3	950	rain	0.4
March, 11	2	963	snow and rain	0.4
12	4	964	rain	0.5
April, 1	7	966	rain	0.9
May, 5	22	976	thunder-shower	0.3
8	19	979	rain	0.8

Table II shows traces of chloride and bromide in surface snow, depending on its distance away from the highway. During the winter, large quantities of salt are strewn on the highways and the salt used on the highway under examination was a NaCl raw salt. This salt impedes plant growth. This examination was carried out to obtain more precise information on the amount and on the way in which the salt is transported from the highway to the nearby surroundings.

Using both MS-IDA and ion selective electrodes, it was seen that the traces of chloride decrease constantly the further away the sample was taken from the highway. The results of both methods were comparable. Even in samples taken at a distance of 50 m, the salt has a distinct influence on the chloride content of the surface snow. Even at a distance of 300 m, the chloride content is still above that of snow which has just fallen (see Table I). It can be concluded that salt reaches the distant surroundings by various means of transport, e.g. by being sprayed, and it is therefore not only the areas near the highway that are endangered.

Reproducibility examinations using MS-IDA on aliquot parts of the sample taken from a distance of 10 m away from the highway showed that MS-IDA achieves a relative standard deviation of 1.3 %. Analogous examinations using an ion selective electrode produced relative standard deviations of 5–11 %. Unlike the traces of chloride, there is no continual decrease in traces of bromide with the distance away from the highway. Values obtained using MS-IDA and the ion selective electrode were not comparable. On an average, results using ion selective electrodes are higher by about a factor of 4. The analysed concentrations are only slightly above the proof limit for the Br^- selective electrode and the electrode also shows that it is sensitive to interference from other ions, e.g. from traces of S^{2-}, which may explain the different analytical values. However, MS-IDA using negative thermal ionization is a selective method because the masses 79 and 81 in the mass spectrum are only occupied by bromine. Owing to the fact that MS-IDA is also an absolute method, the present values obtained by mass spectrometry can be regarded with a greater degree of confidence. This is also supported by the fact that in parallel determinations of traces in samples in the present concentration range, MS-IDA produced a relative standard deviation of 3 % and with the ion selective electrode it was 7–18 %.

TABLE II

Cl^- and Br^- content in snow depending on its distance away from a highway

Distance from highway [m]	Cl^- content [μg/g]		Br^- content [ng/g]	
	MS-IDA	Ion selective electrode	MS-IDA	Ion selective electrode
2	71	68	124	580
10	40	45	79	380
20	32	40	196	430
30	26	31	40	300
40	18	23	351	320
50	13	17	66	220
300	6	11		130

The change of the content of bromide in the samples depending on their distance from the highway, which was not analogous to the change in chloride, shows that the bromide in surface snow must originate from various sources. Using MS-IDA, the bromide content of the road salt was determined at $(136 \pm 3)\,\mu g/g$. As the road salt consists of NaCl, then the traces of Br^- in the snow from this source should be lower on an average by a factor of 10 as compared to the Cl^- values. A reason for higher traces of bromide and for a high variation in concentrations, is probably the bromide in vehicle exhausts which originates from the combustion of petrol additives. In any case, the bromide content is far above that of fresh snow or rain which we analysed at 4–15 ng/g.

TABLE III

Determination of chloride and bromide in aerosol

Sample	Analysed content Cl^- [$\mu g/m^3$]	 Br^- [ng/m^3]
From laboratory air:		
Absorbed by filter	1.74/3.55	12/43
Absorbed in NaOH	0.84/1.79	93/56
From external air:		
Absorbed by filter	0.40/0.95	148/276
Absorbed in NaOH	0.81/1.77	14/20

Aerosols

Table III summarizes the Cl^- and Br^- results of aerosol analyses of laboratory and external air. All the larger aerosol particles were absorbed by the filter (pore size $8\,\mu m$) whereas the smaller particles and the gas were passed through a solution of NaOH, which meant that all the absorbable components were contained in this solution. The quantity absorbed by the filter was between 0.5 and 1.8 mg with a sampled air volume of $11\text{–}20\,m^3$. The Br^- analyses were carried out in two tests at different times independently of each other; Table III shows the results of both tests.

The analysed Cl^- and Br^- contents are in the same range as it was found by other examinations.[6,7,21] It is interesting to note in this connection that the analysed Cl^- in the laboratory air absorbed in NaOH solution is lower than the Cl^- content absorbed in the filter fraction, which is contrary to the results of Br^-. The investigations of external air show an inverse effect. Hence it follows that the analysed chlorine and bromine should be originate from different sources. The aerosol analyses of Br^- in external air show values which allow one to conclude that there was pollution from automobile exhausts, as various publications have pointed out.[21] However, the bromide content which we determined in aerosol from the periphery of Regensburg is far lower compared to aerosols of American towns.[6]

The present results show that MS-IDA can also be applied to aerosol samples to analyse their content of halides. This means that we now have an absolute method in this field of environmental trace analysis which is of great importance for analytical comparisons and for standardization.

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