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Direct determination of halogens in powdered geological and environmental samples using isotope dilution laser ablation ICP-MS

Sergei F. Boulyga*, Klaus G. Heumann

Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

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Abstract

Laser ablation inductively coupled plasma isotope dilution mass spectrometry (LA-ICP-IDMS) with a special laser ablation system for bulk analyses (LINA-Spark^{TM}-Atomiser) was applied for direct determinations of chlorine, bromine, and iodine in rock and sediment samples. Special attention was focused on possible inter-halogen fractionations and analyte/spike isotope fractionations by using LA-ICP-MS and LA-ICP-IDMS, respectively. A variation of Br/Cl and I/Cl element intensity ratios by a factor of 1.3–3 was observed when changing the nebulizer gas flow rate in the range of 0.84–1.0 L min^{-1} and the laser power density in the range of 2–10 GW cm^{-2}, respectively. When using an internal standard for halogen quantification in LA-ICP-MS, this inter-element fractionation can cause systematic errors, which can be avoided by applying the isotope dilution technique. However, at high laser power densities (>5.7 GW cm^{-2} for iodine and >4.0 GW cm^{-2} for bromine and chlorine) the corresponding measured isotope ratio of the isotope-diluted sample deviates significantly from the target value. Under optimised conditions concentrations in the range of 30 μg g^{-1}–16 $\times$ 10^3 μg g^{-1} for chlorine, <2–140 μg g^{-1} for bromine, and <0.1–31 μg g^{-1} for iodine were determined by LA-ICP-IDMS in two sediment reference materials (SRM 1646, SRM 2704) and three rock reference samples (GS-N, Granite; BX-N, Bauxite; DT-N, Disthene), which have not been certified for these halogens. The sediment results agree well within the given uncertainties with indicative values by different methods and the results of the rock samples with those obtained by negative thermal ionisation isotope dilution mass spectrometry. The detection limits of LA-ICP-IDMS are 8 μg g^{-1} for chlorine, 1.7 μg g^{-1} for bromine, and 0.1 μg g^{-1} for iodine.

Keywords: LA-ICP-IDMS; Direct analysis; Powdered samples; Isotope dilution mass spectrometry; Halogen

1. Introduction

Investigations of the geochemical cycle of halogens and the determination of their abundances in meteorites are important topics of halogen trace analysis which require accurate results [1]. Furthermore, halogen analyses are necessary in several fields of technology, for example, gas hydrate exploration, corrosion monitoring of steel reinforced concrete, and semiconductor production.

Halogens are usually determined as their halide ions in aqueous solutions using an ion selective electrode or ion chromatography. However, in the case of solid samples the necessary decomposition or extraction process often leads to substantial and non-reproducible losses of these analytes, independent of the high risk of contamination. In addition, optical atom spectrometric methods are usually not sensitive enough for halogen trace analyses. These analytical problems may be the major reason why none of the many existing rock and sediment reference materials is certified for their chlorine, bromine, or iodine concentration. Instrumental neutron activation analysis (INAA) was often applied in the past as a direct method for halogen trace analyses. However, interferences by high matrix radioactivity after irradiation cause also problems. Radiochemical NAA but also thermal ionisation isotope dilution mass spectrometry (TI-IDMS) had been therefore the preferable choices in the past for accurate determinations of chlorine, bromine, and iodine in geochemical

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* Corresponding author. Tel.: +49 6131 3925326; fax: +49 6131 3925326.
E-mail address: boulyga@uni-mainz.de (S.F. Boulyga).

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and cosmic samples [1]. Both methods are connected with extensive sample preparation steps, which are relatively time-consuming. For TI-IDMS there is also a high risk of contamination.

A direct analytical method like laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), in general, simplifies and shortens the analytical procedure and avoids errors associated with sample preparation. This is useful especially in the case of elements difficult to analyse such as halogens, where volatile products are formed during acid treatment or a high risk of contamination exists. This is especially the case for chlorine with its high natural abundance. During the last decade, the application of LA-ICP-MS has constantly increased and a large number of publications demonstrate the merits of this method for the direct analysis of trace elements in solid samples for almost all fields of science and technology [2–4], including material sciences [5,6], geology, mineralogy and archaeology [7–10] as well as environmental monitoring [11,12]. Despite these advantages and the large experience in different fields of application, however, the mechanisms of laser ablation and its possible influence on the accuracy of results are still being under discussion. According to recent investigations a severe problem in LA-ICP-MS is element fractionation caused by a non-stoichiometric laser ablation and by different ionisation degrees of the analyte in the ICP depending on the ablated aerosol [13–18]. Furthermore, matrix effects can remarkably influence the accuracy and sensitivity of the ICP-MS measurement. Calibration in LA-ICP-MS therefore is a serious problem if no matrix-matched reference material with certified analytes is available. External calibration using non-matrix-matched reference materials cannot guarantee accurate determinations of element concentrations as investigations with certified reference materials have demonstrated [19].

Recently, a combination of LA-ICP-MS with the isotope dilution technique (LA-ICP-IDMS) was developed for trace metal determinations in powdered samples [20–22]. Bulk analysis was performed by using a laser ablation system with high ablation rates (LINA-Spark$^{\text{TM}}$-Atomiser), because this modified system provides high laser power densities and a sufficiently large sampling area by focusing the laser behind the sample surface and by rotating the laser beam within one run in a cycle of 4 mm in diameter. This compensates for possible influences of sample heterogeneities and for possible inhomogeneities of the spike distribution in the sample and thus enables accurate and precise results by LA-ICP-IDMS [20,21]. Element fractionation effects had been avoided by using LA-ICP-IDMS because only an isotope ratio measurement of the isotope-diluted sample is necessary. The chemical form of the analyte in the sample and of the corresponding spike is usually different, so that equilibration between spike and analyte must have taken place during the ablation process. Even if this precondition was fulfilled in the previous studies for trace metal determinations [20–22], fractionation between analyte and spike can be a risk for volatile elements like halogens.

The aim of this work was therefore the development of a LA-ICP-IDMS procedure for a direct and simultaneous determination of chlorine, bromine, and iodine in rocks, sediments and similar samples. This isotope dilution technique must guarantee a laser ablation process without spike/analyte fractionation. In addition, inter-halogen fractionations were investigated for LA-ICP-MS measurements to evaluate possible errors in halogen determinations without the isotope dilution technique.

2. Experimental

2.1. Samples and sample preparation

Two sediment standard reference materials (SRM 1646, Estuarine Sediment; SRM 2704, Buffalo River Sediment) and three rock reference materials (GS-N, granite; BX-N, bauxite; DT-N, disthene), which all are not certified for chlorine, bromine, and iodine, were obtained from the National Institute of Standards and Technology, Gaithersburg, MD, USA, and the Centre de Recherches Petrographiques et Geochimiques in Nancy, France, respectively.

For more detailed information on these reference materials see corresponding internet pages of the National Institute of Standards and Technology and the Centre de Recherches Petrographiques et Geochimiques [23]. For isotope dilution analysis approximately 2 g of the pulverised sample were spiked with about 0.2–0.5 g each of a ^{37}Cl-, ^{79}Br-, and ^{129}I-enriched spike solution and mixed up for 5 min with a Vortex mixer. The amount of added spike was chosen to be in the range of an optimum analyte/spike ratio for the isotope dilution technique [24]. After drying at 75 °C the isotope-diluted powder was pressed to pellets of 20 mm in diameter. A more detailed description of the preparation of the pellets is given elsewhere [20]. Pellets from non-spiked samples were used for the determination of the mass discrimination in LA-ICP-MS measurements under the corresponding conditions.

2.2. Spike solutions

Spike solutions of ^{37}Cl (92.65 % of ^{37}Cl and 7.35% of ^{35}Cl), ^{79}Br (91.18% of ^{79}Br and 8.82% of ^{81}Br) and ^{129}I (86.08% of ^{129}I and 13.92% of ^{127}I) were prepared from corresponding isotopically enriched sodium halide salts, purchased from Monsanto Research Corporation (Dayton, OH, USA) and NEN Chemicals GmbH (Dreieich, Germany). The isotopic composition of the spike solutions was determined by ICP-MS with corrections for mass discrimination (except iodine) by measuring corresponding standard solutions of known (natural) isotopic composition. For IDMS determinations, the uncorrected isotope values of the spike, the sample and the isotope-diluted sample were used. It has been demonstrated in a previous investigation that this procedure compensate possible errors by mass discrimination so that accurate results can be obtained without correcting any data

Table 1
Optimum operational parameters for the ICP-MS and the laser ablation system

ICP-MS	Element 2
rf power (W)	1320
Cooling gas flow rate (L min^{-1})	16.0
Auxiliary gas flow rate (L min^{-1})	0.95
Nebuliser gas flow rate (L min^{-1})	0.96
Mass resolution	4000 (medium)
Number of replicates	30
Analysis time (min)	6
Laser ablation system	LINA-Spark$^{\text{TM}}$
Wavelength (nm)	1064
Pulse energy (mJ)	97
Pulse duration (ns)	7
Laser focus	−15 mm
Spot diameter (μm)	700
Power density (GW cm^{-2})	3.6
Laser ablation frequency (Hz)	10
Scanning mode	Spot scan
Ablated area	4 mm diameter

[25]. Spike concentrations were determined by reverse IDMS using corresponding standard solutions of natural isotopic composition. If necessary these stock spike solutions were diluted with Milli-Q water to a concentration which fits best the spiking procedure.

2.3. LA-ICP-MS instrumentation

A double-focusing sector-field ICP-MS (Element 2, ThermoElectron, Bremen, Germany) was used under the conditions listed in Table 1. A mass resolution of 4000 was applied to avoid possible interferences by molecular ions. For laser ablation a LINA-Spark$^{\text{TM}}$-Atomiser system (LSA Sarl, Cully, Switzerland) was used. This ablation system, especially constructed for bulk analyses, consists of a Nd:YAG laser working in the Q-switched mode at its fundamental IR wavelength of 1064 nm. The sample is fixed at top of the ablation chamber and ablated from below. The laser beam is defocused (∼15 mm behind the sample surface) and moves circularly over the sample surface by means of a motor-driven lens, which is mounted on a *xy*-stage. The ablated sampling area has a diameter of roughly 4 mm, which is usually large enough to compensate for sample inhomogeneities. Further details of the applied LA system and its optimisation can be found elsewhere [5,20].

3. Results and discussion

3.1. Sensitivity and precision of LA-ICP-MS measurements

Because of the relatively high first ionisation potentials of halogens (12.97, 11.82 and 10.45 eV for Cl, Br and I) the ionisation efficiency in the plasma is low. From the results of an earlier work using a prototype 193 nm ArF excimer laser system and a quadrupole ICP-MS a sensitivity for $^{35}\text{Cl}^+$ of less than 1 cps/μg g^{-1} was obtained [26]. Due to the high ablation rate provided by the LINA-Spark$^{\text{TM}}$-Atomiser system the amount of ablated material is higher by several orders of magnitude in comparison to commonly used laser ablation systems. This results in higher sensitivities by, at least, two orders of magnitude [27]. In this work a sensitivity of 110, 1300, and 10 200 cps/μg g^{-1} was observed for $^{35}\text{Cl}^+$, $^{81}\text{Br}^+$ and $^{127}\text{I}^+$, respectively, at an ablation frequency of 2 Hz and a nebuliser gas flow rate of 0.96 L min^{-1} (Figs. 1 and 2). Increasing ablation frequencies of up to 10 Hz further improve the sensitivity of all halogen ions by a factor of more than two as is shown for chlorine in Fig. 2.

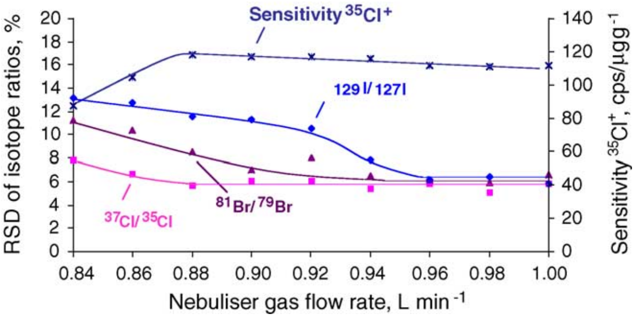

Fig. 1. $^{35}\text{Cl}^+$ ion sensitivity and precision of $^{37}\text{Cl}/^{35}\text{Cl}$, $^{81}\text{Br}/^{79}\text{Br}$ and $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurements by LA-ICP-MS dependent on the nebuliser gas flow rate (SRM 1646 spiked with ^{37}Cl, ^{79}Br and ^{129}I; laser ablation frequency 2 Hz).

Due to the important role of the precision of isotope ratio measurements in IDMS, the influence of different experimental parameters on the corresponding relative standard deviation (RSD) was investigated. Fig. 1 presents the dependence of the precision for $^{37}\text{Cl}/^{35}\text{Cl}$, $^{81}\text{Br}/^{79}\text{Br}$, and $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurements on the nebuliser gas flow rate during ablation of the spiked sediment SRM 1646. A significant improvement of the relative standard deviation by a factor in the range of 1.3–2 could be achieved by increasing the nebuliser gas flow rate from 0.84 to 0.96 L min^{-1} (at a constant ablation frequency of 2 Hz), although the sensitivity of the halogen signals (in Fig. 1 demonstrated for chlorine)

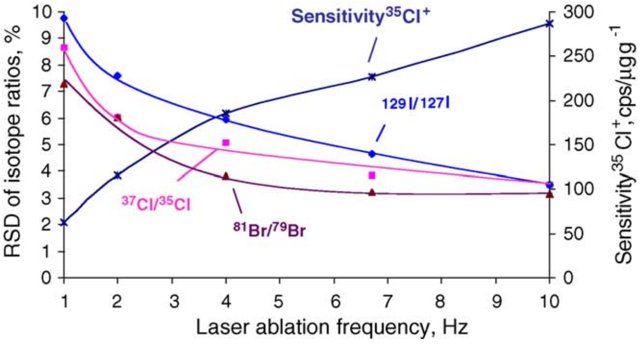

Fig. 2. $^{35}\text{Cl}^+$ ion sensitivity and precision of $^{37}\text{Cl}/^{35}\text{Cl}$, $^{81}\text{Br}/^{79}\text{Br}$ and $^{129}\text{I}/^{127}\text{I}$ isotope ratio measurements by LA-ICP-MS dependent on the laser ablation frequency (spiked SRM 1646; nebuliser gas flow rate 96 L min^{-1}).

remain nearly constant. Increasing ablation frequencies of up to 10 Hz improve the homogeneity of the ablated aerosol and, hence, also the precision of isotope ratio measurements from 7–10% to about 3% RSD (Fig. 2).

3.2. *Inter-element fractionation of halogens in LA-ICP-MS measurements*

The laser ablation process as well as the excitation of the sample aerosol in the ICP is relatively complex and different effects can cause inter-element fractionation. In the present work, a significant increase of the Br/Cl and I/Cl element intensity ratios was observed by increasing nebuliser gas flow rates in the range of 0.84–1.00 L min^{-1} (Fig. 3; the plotted element ratios were calculated by measuring the ion intensity of one isotope per element and correcting for the corresponding total halogen intensity by the known natural isotopic abundances). This effect is, on the one hand, due to a shorter residence time of the aerosol in the ICP with increasing nebuliser gas flow rates, which more likely reduces the ionisation degree of elements with higher ionisation energies. On the other hand, a higher nebuliser gas flow rate introduces more aerosol particles into the ICP, which alters the mass discrimination of ions by a higher ion density in the plasma. This strong inter-halogen fractionation demonstrates that LA-ICP-MS analyses with external calibration by using an element with known concentration in the sample and calibrant can easily cause wrong results.

Fig. 4 presents the sensitivity for chlorine ions as well as the intensity ratios Br/Cl and I/Cl as a function of the laser power density. Increasing power densities in the range of about 2–5 GW cm^{-2} result in an increase of the sensitivity for all measured halogens which afterwards decreases slightly up to 9.5 GW cm^{-2}, as is shown for chlorine in Fig. 4. At laser power densities >5 GW cm^{-2} the decrease of sensitivity is probably caused by self-shielding of the laser irradiation by the argon plasma and by the ablated material in the ablation plume. However, over the whole investigated range the I/Cl and Br/Cl element intensity ratios continuously decrease with increasing laser power density, which means that chlorine ions are more enhanced than those of the other two halogens. This might be due to the fact that iodine and bromine containing compounds are more easily evaporated in an atomised form, whereas chlorine species with their higher bond energies require higher laser energy to be atomised. However, different other effects during the complex laser ablation process may also cause the observed inter-halogen fractionation.

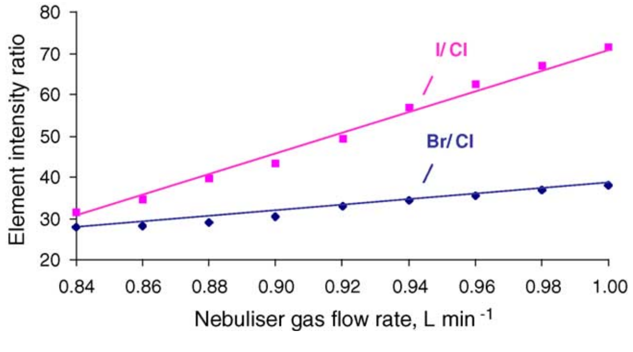

Fig. 3. Dependence of the element intensity ratios Br/Cl and I/Cl of LA-ICP-MS measurements on the nebuliser gas flow rate (unspiked SRM 1646; Br/Cl ratio is enhanced by a factor of 2 for better presentation; the plotted element ratios were calculated by measuring the ion intensity of one isotope per element and correcting for the corresponding total halogen intensity by the known natural isotopic abundances).

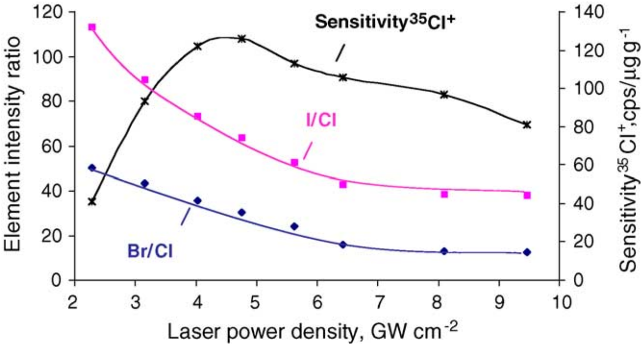

Fig. 4. Dependence of the $^{35}\text{Cl}^+$ ion sensitivity and the element intensity ratios Br/Cl and I/Cl of LA-ICP-MS measurements on the laser power density (unspiked SRM 1646; Br/Cl ratio is enhanced by a factor of 2 for better presentation).

3.3. *Analyte/spike isotope fractionation in LA-ICP-IDMS measurements*

The possible influence of element fractionation on the calibration of trace metal determinations by LA-ICP-MS could be avoided by applying the isotope dilution technique [20,21]. However, in case of the volatile halogens, the usually different chemical form of the spike and analyte may alter their evaporated fraction during the ablation process as well as their degree of ionisation in the ICP. Compounds with high evaporation enthalpies and binding energies or those embedded in the aerosol particles may probably show lower ionisation efficiencies so that the composition of the isotope-diluted sample is not correctly represented by the measured isotope ratio. The isotope ratios $^{37}\text{Cl}/^{35}\text{Cl}$, $^{79}\text{Br}/^{81}\text{Br}$, and $^{129}\text{I}/^{127}\text{I}$ (spike isotope divided by reference isotope) of an isotope-diluted sample (SRM 1646) were therefore followed in dependence on the nebuliser gas flow rate in the range of 0.9–1.0 L min^{-1}. No variation of the isotope ratios was observed within the precision of the isotope ratio measurement of about 3% RSD.

In contrast to this, constant isotope ratios of the isotope-diluted sample were only measured in a limited range of the laser power density (Fig. 5; solid lines). Decreasing isotope ratios, which are identical with a suppressed detection of the spike compound compared with the sample analyte, were observed for all halogens at high laser power densities. A decreasing isotope ratio was measured for bromine and chlorine from about 4 GW cm^{-2} on, for iodine from about 5.7 GW cm^{-2} on. On the other hand, in the case of low laser power densities an enhanced detection of the spike

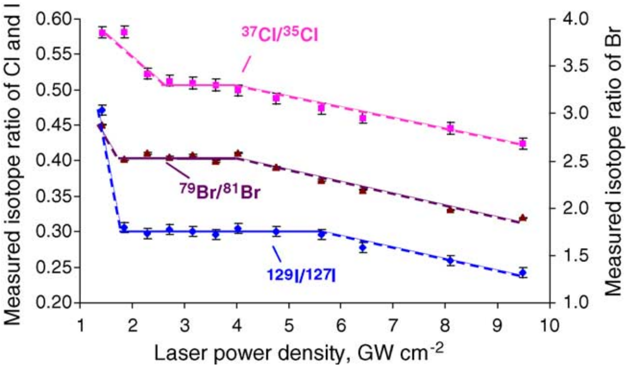

Fig. 5. Measured isotope ratios ^{37}Cl/^{35}Cl, ^{79}Br/^{81}Br and ^{129}I/^{127}I of an isotope-diluted sample as a function of the laser power density (SRM 1646; nebuliser gas flow rate 0.96 L min^{-1}; laser ablation frequency 2 Hz).

was found (see measured isotope ratios, for example, at 1.4 GW cm^{-2} in Fig. 5). This means that a constant isotope ratio of the isotope-diluted sample is only available in the range of 2–5.7 GW cm^{-2} for iodine, 2–4 GW cm^{-2} for bromine, and 2.7–4 GW cm^{-2} for chlorine. To allow multi-halogen determinations within one run by LA-ICP-IDMS a laser power density of 3.6 GW cm^{-2} was therefore chosen. This condition also fits best the true isotope ratio of the isotope-diluted sample. This was confirmed by LA-ICP-IDMS results obtained under this condition which agree well with indicative values [28] (see Table 2).

The enhanced detection of the spike at low laser power densities may be due to a preferred evaporation of the spike compounds from the isotope-diluted sample. On the other hand, a suppressed detection like that one measured for the halogen spikes at high laser power densities was recently also observed by Kuhn and Günther for zinc during LA-ICP-MS measurements of a Zn/Cu alloy [29].

Table 2
Halogen determinations by LA-ICP-IDMS in sediment and rock samples and comparison with indicative values from [28,30–32]

Sample	Concentration (µg g^{-1})	Indicative value (µg g^{-1})
Chlorine		
SRM 1646	16100 ± 1900	14200 ± 800 (5[a])
SRM 2704	132 ± 18	116 ± 28 (3[a])
GS-N	407 ± 57	442 ± 3.3[b]
DT-N	30 ± 10	27.0 ± 0.5[b]
BX-N	30 ± 4	27.7 ± 0.3[b]
Bromine		
SRM 1646	137 ± 15	115 ± 10 (10[a])
SRM 2704	5.1 ± 0.7	6.0 ± 0.4 (11[a])
GS-N	2.56 ± 0.37	2.3 ± 0.1[b]
DT-N	<1.7	0.058 ± 0.012[b]
BX-N	<1.7	0.983 ± 0.014[b]
Iodine		
SRM 1646	31.0 ± 1.0	33 ± 2 (6[a])
SRM 2704	2.6 ± 0.2	2.1 ± 0.3 (3[a])
GS-N	<0.1	0.031 ± 0.003[b]
DT-N	<0.1	0.063 ± 0.002[b]
BX-N	3.0 ± 0.2	2.52 ± 0.05[b]

[a] Number of individual values from different reports and analytical methods used to calculate this indicative value.
[b] Data from NTI-IDMS determinations.

3.4. LA-ICP-IDMS determinations in sediment and rock samples

The results for chlorine, bromine, and iodine by LA-ICP-IDMS under optimised conditions (Table 1) for two sediment and three rock reference materials, not certified for the corresponding halogens, are summarised in Table 2. The given standard deviations result from three independent analyses. The chlorine concentrations vary from 30 µg g^{-1} to 16×10^3 µg g^{-1}, whereas the corresponding bromine and iodine concentrations are much lower and range from <1.7 to 137 µg g^{-1} and from <0.1 to 31 µg g^{-1}, respectively. The bromine and iodine concentrations in two rock reference materials were found to be below the detection limit of 1.7 and 0.1 µg g^{-1}. The detection limit was calculated from the mass spectrum of the blank argon gas by $(m_b + 3s_b)/S$, where m_b is the mean value of the blank intensity in cps, s_b the standard deviation of five independent measurements of the blank in cps, and S is the sensitivity. Chlorine concentrations of the investigated samples were always above the detection limit of 8 µg g^{-1}.

In principle, the observed analyte/spike fractionation and the different optimisation procedures carried out during the development of the LA-ICP-IDMS require an evaluation of this method. Because of a lack of analytical methods for accurate halogen determinations in geological and related samples, no certified reference material exists at the moment. The investigated samples were therefore selected under the aspect that, according to our knowledge, reliable indicative values were available from the literature. In the last column of Table 2 corresponding data are listed for the two sediments which were obtained from a compilation of different references [28]. The reference values for the rock samples were obtained from determinations by negative thermal ionisation isotope dilution mass spectrometry (NTI-IDMS) [30–32]. The LA-ICP-IDMS data mainly agree well with the listed indicative values so that, in general, accurate results can be assumed. However, the precision of the NTI-IDMS determinations is much better than that by LA-ICP-IDMS, which may be due to the higher influence of sample inhomogeneities and the relatively small sample volume analysed by laser ablation. On the other hand, sample preparation for TI-IDMS analyses are much more complicated and time-consuming compared with the relatively simple and time-efficient LA-ICP-IDMS method. Recently Moser et al. have shown by wet-chemical IDMS analysis of platinum group elements that the contribution of sample preparation and heterogeneity to the combined IDMS uncertainty exceeds the contribution of all other uncertainty components [33]. In the case of LA-ICP-IDMS, the relative contribution of sample heterogeneity is even higher because of a significantly lower sampling volume which is analysed. Therefore, the given standard deviations of the LA-

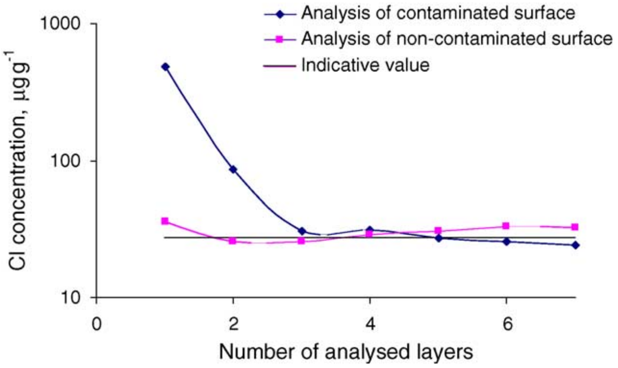

Fig. 6. Chlorine concentrations determined by LA-ICP-IDMS at a contaminated and non-contaminated surface of the same isotope-diluted BX-N sample in seven consecutive layer-by-layer analyses.

ICP-IDMS results in Table 2 mainly represent the uncertainty caused by sample heterogeneity.

In the case of analysing samples with low chlorine concentrations, a pre-ablation of the sample pellets is recommended to eliminate possible surface contamination which can otherwise lead to wrong results as shown in Fig. 6 for a contaminated BX-N sample. Two series of seven consecutive layer-by-layer laser ablation analyses were performed on opposite surfaces of the same isotope-diluted rock sample, where one surface was obviously contaminated during pressing. Whereas the chlorine concentration determined at the non-contaminated surface by LA-ICP-IDMS agrees well with the indicative value by NTI-IDMS from the first layer on, the contaminated side of the pellet shows much too high values in the first two analysed layers but afterwards it reaches the indicative value.

4. Conclusion

LA-ICP-IDMS offers the possibility for direct and simultaneous determination of chlorine, bromine, and iodine in powdered sediments, rocks and related geological and environmental samples at concentration levels down to the low $\mu g\, g^{-1}$ level and less for chlorine, bromine and iodine, respectively. Although a fractionation between analyte and spike was observed for isotope-diluted samples during the ablation process at high laser power densities, appropriate experimental conditions could be found where no fractionation was observed and the LA-ICP-IDMS results agreed well with reference values from the literature. Recently, it could be demonstrated that not only the LINA-Spark^{TM}-Atomiser system applied in this work is able to produce accurate results for powdered samples by LA-ICP-IDMS but also commonly used laser ablation systems with only a few restrictions in the level of detection limits [27]. This isotope dilution technique therefore opens the possibility in the future for time-effective and accurate halogen determinations in many matrices. The application of LA-ICP-IDMS may also allow the first certification of chlorine, bromine, and iodine in a reference material.

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