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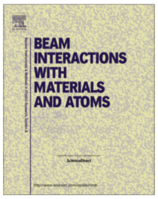

Interlaboratory study of the ion source memory effect in ^{36}Cl accelerator mass spectrometry

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ABSTRACT

Understanding and minimization of contaminations in the ion source due to cross-contamination and long-term memory effect is one of the key issues for accurate accelerator mass spectrometry (AMS) measurements of volatile elements. The focus of this work is on the investigation of the long-term memory effect for the volatile element chlorine, and the minimization of this effect in the ion source of the Dresden accelerator mass spectrometry facility (DREAMS). For this purpose, one of the two original HVE ion sources at the DREAMS facility was modified, allowing the use of larger sample holders having individual target apertures. Additionally, a more open geometry was used to improve the vacuum level. To evaluate this improvement in comparison to other up-to-date ion sources, an interlaboratory comparison had been initiated. The long-term memory effect of the four Cs sputter ion sources at DREAMS (two sources: original and modified), ASTER (Accélérateur pour les Sciences de la Terre, Environnement, Risques) and VERA (Vienna Environmental Research Accelerator) had been investigated by measuring samples of natural ^{35}Cl/^{37}Cl-ratio and samples highly-enriched in ^{35}Cl (^{35}Cl/^{37}Cl$\sim$999). Besides investigating and comparing the individual levels of long-term memory, recovery time constants could be calculated. The tests show that all four sources suffer from long-term memory, but the modified DREAMS ion source showed the lowest level of contamination. The recovery times of the four ion sources were widely spread between 61 and 1390 s, where the modified DREAMS ion source with values between 156 and 262 s showed the fastest recovery in 80% of the measurements.

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1. Introduction

Accelerator mass spectrometry (AMS) is an ultrasensitive method for the measurement of isotopic ratios. Usually, ratios of radioactive nuclei to their stable isotopes are measured [1–3]. Due to the direct detection and counting of the radioisotopes, AMS does not depend primarily on radioactive decay parameters such as branching ratios and half-lives. The suppression of interfering molecular isobars enables, depending on the measured isotope, the measurement of isotopic ratios down to 10^{-16}–10^{-12} which cannot be achieved by any other analytical technique. Therefore, AMS covers a wide spectrum of applications which range from dating organic material to geomorphology and astrophysical studies [1–3].

Chlorine-36 (half-life = $(3.013 \pm 0.015) \times 10^5$ a [4]) is a cosmogenically and anthropogenically produced radionuclide. It is commonly used for groundwater dating (e.g. [5,6]), surface rock exposure dating (e.g. [7]), bomb peak studies (e.g. [8]) and extra-terrestrial material and cosmic ray variations studies (e.g. [9]). Due to the necessity of reaching the charge state 5+ to insure an unambiguous characterization and detection of ^{36}Cl, AMS measurements of ^{36}Cl were usually performed with large accelerators capable of producing terminal voltages of at least 5 MV that in addition provide the necessary energy for separating ^{36}Cl from the naturally superabundant ^{36}S. Recently, Martschini et al. [10,11] showed that measurements of ^{36}Cl with sufficient sulfur suppression are also possible at lower energies.

Besides the suppression of sulfur, a well working ion source is crucial to gain high-quality data in ^{36}Cl-AMS. AMS ion sources are usually based on the Middleton concept of sputtering negative ions with Cs [12,13]. Negative ions are emitted from the sample

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material by sputtering with Cs^+ -ions and using neutral Cs deposited on the cooled target as electron donator. According to Middleton [13] and Kilius et al. [14] the requirements for a good working AMS ion source are:

- High and stable current.
- Low emittance.
- High ionization efficiency.
- Low memory effect.
- Fast sample changing.

Chlorine, as a halogen, easily forms negative ions resulting in a very high sputtering efficiency, which is, according to Middleton [15], in the range of 16%. This means that the high-efficiency and high-current requirements are easily satisfied for Cl. With sample changing times of a few seconds, the criteria of fast sample changing is also met in up-to date ion sources. Despite the high electron affinity, most of the sputtered Cl, however, remains neutral in the ion source [15]. This gaseous neutral Cl either stagnates in the ion source, is pumped or condensates on cold surfaces in the ion source. This implies the build-up of an ion source Cl reservoir, which isotopic ratio is a mixture of the ratios of the previously sputtered targets and may affect all following measurements. This so-called long-term memory effect has to be considered in addition to the short-term memory effect that concerns the contamination of one sample by the immediately preceding one. These ion source memory effects (short- and long-term) were recently discussed in Wilcken et al. [16,17], Arnold et al. [18] and Finkel et al. [19]. Based on these works, we focused on optimizing the High Voltage Engineering (HVE) SO110 ion source at the Dresden accelerator mass spectrometry (DREAMS) facility for the measurement of volatile elements with the aim of minimizing the long-term memory effect. The performance of the modified ion source were then compared to other up-to-date ion sources.

Minimizing the long-term memory effect is also crucial for AMS measurements of other volatile elements such as iodine, i.e. $^{129}I/^{127}I$ ratios, and therefore the performed study also has important implications for smaller machines, which do not measure ^{36}Cl. However, chlorine unlike iodine has two stable isotopes, i.e. ^{35}Cl and ^{37}Cl, which makes Cl more pertinent considering the measurement procedures developed for this work. The focus of this work is therefore the measurement of the ion source long-term memory effect using the two stable isotopes of chlorine.

2. Experimental

In order to determine the long-term memory effect, a protocol using AgCl-samples of different $^{35}Cl/^{37}Cl$-ratios was developed. Measuring the $^{35,37}Cl$ currents avoids the limitations linked to low counting statistics of the rare radionuclide, and thus allows to perform precise measurement of the change of the $^{35}Cl/^{37}Cl$-isotopic ratios over time for the determination of recovery times. This protocol was followed to compare the long-term memory effect of the ion sources of the following AMS facilities:

- DREAMS (modified and original HVE ion source).
- ASTER (modified HVE ion source).
- VERA (modified National Electrostatics Corporation ion source).

2.1. Investigated samples

For the measurement of the long-term memory effect AgCl-samples with natural $^{35}Cl/^{37}Cl$-ratio of $r_{nat} = 3.127$ and samples highly-enriched in ^{35}Cl with a $^{35}Cl/^{37}Cl$-ratio of $r_{enr} = 999$ (Sigma Aldrich, CAS number: 20510-55-8) were used.

The samples with natural ratio were precipitated from two dilute HNO_3- solutions, one containing Ag^+ as $AgNO_3$ and the second Cl^- as NH_4Cl. The AgCl-samples enriched in ^{35}Cl were precipitated from the same solution containing Ag^+ and from a second solution containing the dissolved NaCl material from Sigma Aldrich. The typical AgCl-sample mass was 12 mg. All precipitated samples were washed individually three times with 5 ml of deionised H_2O and dried for several hours at 80 °C. The samples enriched in ^{35}Cl and the samples of natural isotopic composition were prepared and dried separately. The sample preparation of all samples was done at the chemistry laboratory of DREAMS. The pressing of the sample material into the sample holders was done at the particular facilities.

The AgCl-samples were pressed into copper sample holders for the measurements at both DREAMS ion sources and into Ni-target holders for the measurements at ASTER. Ni 201 by CLAL-MSX was found to have low sulfur content [19] and therefore is used as material for the sample holders at ASTER. The AgCl-samples for the measurement at VERA were pressed into the conical cavity of Cu sample holders. Due to its low sulfur content AgBr is used as backing material in the sample holders at VERA.

2.2. AMS

The long-term memory effect of the modified HVE SO110 and the original SO110 ion sources, both at the DREAMS [20] facility, the modified HVE SO110 ion source at Accélérateur pour les Sciences de la Terre, Environnement, Risques (ASTER) [21] and the modified National Electrostatics Corporation (NEC) MC-SNICS (Multi Cathode Source of Negative Ions by Caesium Sputtering) at the Vienna Environmental Research Accelerator facility (VERA) [22,23] was measured. Additionally, to the in-house measurements with the modified DREAMS SO110 ion source and the original one, the study of the long-term memory at the ASTER- and the VERA-facility allowed us to compare our modified ion source design to the ion source designs of both AMS-facility suppliers, NEC and HVE.

DREAMS and ASTER both are based on a Tandetron type accelerator from HVE. The DREAMS-facility is equipped with a 6 MV Tandetron and the facility is used for AMS measurements of ^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{129}I as well as for ion beam analytics and high-energy ion implantation [20]. AMS measurements of Cl were performed with the original SO110 ion source of HVE and the modified DREAMS ion source based on this model, both shown in Fig. 1.

ASTER is equipped with the 5 MV model and went operational in 2007 [24]. In contrast to DREAMS, it is a designated AMS-facility and was designed for routine measurements of ^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca and ^{129}I [18,21]. At ASTER, a modified HVE SO110 ion source designed for the measurement of volatile elements is used for Cl- and I-AMS [18,19]. The design of this ion source and the sample holders are also aiming in the reduction of the cross-contamination and the long-term memory effect [19].

At DREAMS as well as at ASTER the maximal terminal voltage of 6 MV and 5 MV, respectively, is used for Cl-AMS and the 5+ charge state is chosen for the current measurement. For the sequential injection of $^{35,36,37}Cl^-$ into the accelerator a fast-bouncing system with a repetition rate of 90 Hz is used [25]. The fast bouncing is synchronized to a gated measurement of the $^{35,37}Cl^{5+}$ currents in two off-set Faraday cups behind the high-energy analysing magnet [25]. The high repetition rate suppresses varying isotopic ratios caused by fast ion source output fluctuations and the gated current measurement together with a fast blanking steerer allow injection periods for the stable isotopes as short as 100 μs [25].

VERA is a facility mainly dedicated to AMS, based on a NEC 3 MV tandem accelerator. It went operational in 1996 [22] and since then was continuously upgraded [23,26–28], allowing to measure a broad range of radionuclides. The VERA-facility has

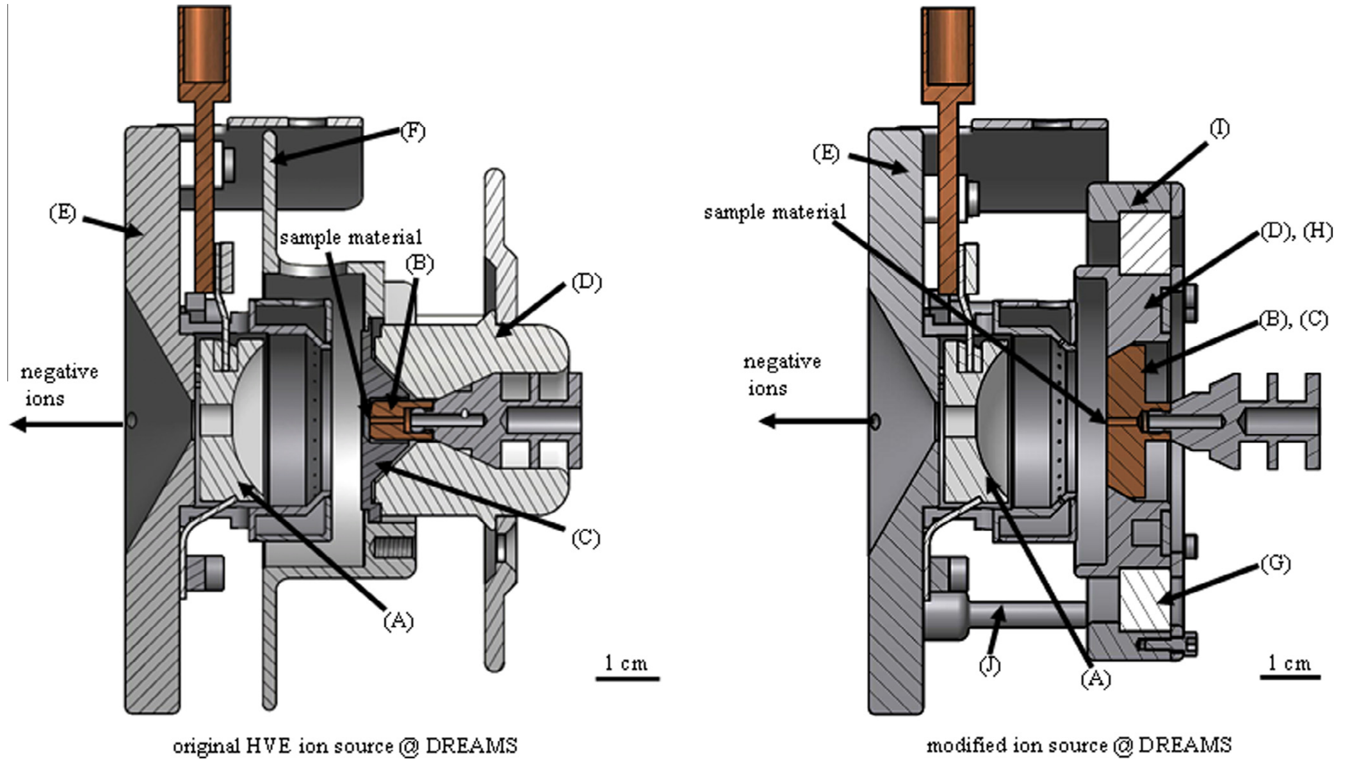

Fig. 1. Schema of the two DREAMS ion sources. The main differences are the more open geometry and the bigger sample holders. The figures show the main parts of the ion sources: (A) ionizer, (B) sample holder, (C) target aperture, (D) sample cooling and positioning system, (E) base plate, (F) shielding for insulators, (G) insulators (not seen in the original ion source as they are not in the intersecting plane), (H) inner ring, on target potential (−29 kV), (I) outer ring on extraction potential (−25 kV) and (J) stainless steel cylinders.

two ion sources, one MC-SNICS, which was modified as described in Priller et al. [29] and one MC-SNICS II [28]. The measurements for this work were performed with the modified MC-SNICS. Cl is usually measured with a terminal voltage of 3 MV in the charge state 7+, which is achieved by C-foil stripping. A multi-beam switcher in front of the low-energy magnet sequentially injects $^{35,36,37}Cl^-$ into the accelerator or $^{35}Cl^-$ into an off-set Faraday cup on the low-energy side by applying additional voltages to the beam, with a repetition rate of several Hz. The $^{35}Cl^-$ current is measured in an off-set Faraday cup on the low-energy side. The $^{35,37}Cl^{7+}$ currents are measured in two off-set Faraday cups after the analyzing magnet.

As samples with different $^{35}Cl/^{37}Cl$-ratios were used for the experiments, ^{36}Cl was not measured. Nevertheless, it should be mentioned that as we used standard sequential injection for chlorine, ^{36}Cl was injected into the accelerator more than 90% of the time. For reason of completeness, it should also be mentioned that at DREAMS and ASTER a 1 μm thick silicon nitride foil and a subsequent energy separation with a 35° ESA is used for the suppression of ^{36}S. After this post-acceleration stripping foil the 11+ charge state at DREAMS, and the 10+ charge state at ASTER is chosen for the final detection and separation of ^{36}Cl and ^{36}S in a four-anode ionization chamber. Isobutane is used as counting gas. At VERA a multi-anode ionization chamber with isobutane as counting gas is used as detector.

The specifications of the three facilities are summarized in Table 1.

2.3. Ion source modifications at DREAMS

In order to minimize the long-term memory effect the original HVE SO110 ion source was modified. Fig. 1 shows the original HVE ion source and the modified one.

Two major modifications had been performed: first, larger sample holders (Fig. 1(B)) had been constructed. Second, the modified ion source has a more open geometry. In the case of the original HVE ion source, sputtered material is deposited on the cooled target aperture (Fig. 1(C)) and remains in the ion source when samples are changed. The deposited material can be resputtered and thus affects all following measurements. By using larger sample holders, each sample holder having its own aperture, the resputtering of most of the deposited material, i.e. material deposited near the target, is avoided because this material is extracted with its individual sample holder. To allow the use of the new sample holders (24 mm in diameter instead of 6 mm), the sample cooling and positioning system was also modified (Fig. 1(D)).

In the original ion source, cylindrical insulators are used to fix the sample cooling and positioning system (Fig. 1(D)) to the base plate (Fig. 1(E)), which is set to a different electric potential. These insulators are shielded from the Cs-vapor (Fig. 1(F)). In the modified ion source, shorter insulators (Fig. 1(G)) are used and the shielding is removed to achieve a more open geometry. These new insulators fix and center the inner ring (Fig. 1(H)) to the outer ring (Fig. 1(I)) of the new target positioning system. The outer ring is fixed to the base plate by stainless steel cylinders (Fig. 1(J)). The whole ion source head is set to an electric potential of −25 kV. Additionally, a voltage of −4 kV is applied to the inner ring and the target.

The more open geometry of the ion source is aiming at the improvement of the vacuum level in the ion source by more efficient pumping and thus at the reduction of the memory effect due to the gas remaining from previously sputtered targets.

2.4. Measurement protocol

An appropriate measurement procedure allowing to determine the parameters that characterize the level of the long-term

Table 1
Specifications and measurement parameters of AMS-facilities.

	Modified DREAMS	Original DREAMS	VERA	ASTER
Ion source	Modified SO110 (HVE)	SO110 (HVE)	Modified MC-SNICS (NEC)	Modified SO110 (HVE)
Sample holder material	Cu	Cu	Cu	Ni
Sample material	AgCl	AgCl	AgCl with AgBr-backing	AgCl
Time sputtering natural Cl targets before experiment (tuning and other tests) (h)	4.5	5.0	20	2.5
Sputter voltage (kV)	4.0	4.0	3.0	3.5
Ionizer power (W)	198	143	80–120 variable, feedback from target current	332
Caesium temperature (°C)	80–85	80	148	103
Extraction voltage (kV)	25	25	9	26
Additional preacceleration voltage (kV)	–	–	58	–
Charge state (stripper)	5+ (Ar-gas)	5+ (Ar-gas)	7+ (C-foil)	5+ (Ar-gas)
Particle energy after accelerator (MeV)	36	36	24	30
Average ^{35}Cl particle current on samples with natural ratio (μA)	2.0	4.2	0.7	3.4
Measurement ranges Faraday cups (natural samples) ^{35}Cl | ^{37}Cl (μA)	100 | 10	100 | 10	20 | 10	100 | 10
Measurement ranges Faraday cups (enriched samples) ^{35}Cl | ^{37}Cl (μA)	100 | 10	100 | 10	20 | 0.25	100 | 10
Repetition rate of current measurements natural samples | enriched samples (Hz)	90 | 90	90 | 90	4.8 | 4.5	90 | 90
Life-time of run (enriched samples) (s)	1000	1000	1222	1000
Real-time of run (enriched samples) (s)	1261–1281	1261–1282	1372–1379	1145–1150
References	This work	[20]	[22,23,26–28]	[18,19,21,24]

memory effect in the ion sources and the time needed to recover initial nominal ratios from contaminated sample ratios is needed. The principal measurement procedure was rather simple:

(1) Tuning of the AMS-system with natural Cl-ratio samples.
(2) Sputtering an enriched sample roughly 21 min while following the temporal evolution of the ^{35}Cl/^{37}Cl-ratio.
(3) Sputtering four natural ^{35}Cl/^{37}Cl-ratio samples roughly 21 min each to contaminate the ion source with natural ^{35}Cl/^{37}Cl-ratio material.
(4) Following during roughly 21 min the temporal evolution of the ^{35}Cl/^{37}Cl-ratio of the initially sputtered enriched sample (equal to step 2).
(5) Repeating the sputtering of four natural ^{35}Cl/^{37}Cl-ratio samples roughly 21 min each (equal to step 3).

With the original DREAMS -, the ASTER - and the VERA ion source, step 2 and 3 were repeated until the enriched sample was measured 12 times. The measurement at the modified DREAMS ion source was aborted during the 6th turn due to problems with the electrical stability of the ion source.

At DREAMS and ASTER, due to fast-bouncing, both ^{35}Cl and ^{37}Cl currents are measured during 100 μs at a repetition rate of 90 Hz. In the remaining time mass 36 was injected into the accelerator. The current measurements are averaged over an adjustable time period (block) which duration was set to 10 s (one data point for ^{35}Cl/^{37}Cl-ratio per block). The measurement duration for each sample was set to 100 blocks. The settings for the Faraday cups were the same for all targets. To determine the sensitivity of the Faraday cup amplifiers at DREAMS, direct current signals generated by a picoampere source were measured in the Faraday cups over the 1 μA and 10 μA-range. In the 10 μA-range, signals of 10 nA, 20 nA and 50 nA were underestimated by ~3%, ~1.5% and ~0.5%, respectively. The measured ^{37}Cl currents at DREAMS and ASTER were in this range. Nevertheless, this additional uncertainty was not considered in the following evaluations because it does not change the final outcome.

At VERA, a run is subdivided into cycles. During each cycle, the ^{35}Cl current on the low-energy side, the ^{35}Cl and ^{37}Cl currents on the high-energy side and usually the number of ^{36}Cl counts in the detector are measured once (one data point for ^{35}Cl/^{37}Cl-ratio per cycle). For the enriched samples the cycle duration was set to 222.2 ms and the measurement time to 5500 cycles. For the natural samples the cycle duration was set to 207.7 ms and the measurement time to 5900 cycles.

The life-times and real-times for the runs on the enriched samples are shown in Table 1.

At VERA the settings of the amplifier of the high-energy Faraday cup measuring the ^{37}Cl current was independently optimized for the samples with natural ratio and the ^{35}Cl-enriched samples.

3. Data evaluation

Due to the different time structure of the raw data, the data evaluation at VERA was slightly different from the evaluations at ASTER and DREAMS.

3.1. Data evaluation DREAMS and ASTER

Only the blocks during which the current is stable and in the range of the typical currents given in Table 1 were taken into account for the evaluation (see Fig. 2). This condition excluded the turns 9–12 measured with the original DREAMS ion source and the turns 6–12 measured at ASTER from the data evaluation. Additionally, for both DREAMS ion sources raw data measured in several blocks on the ^{35}Cl-enriched target was excluded from the data evaluation, because the measurement range of the Faraday cup measuring the ^{37}Cl^{5+} current was manually changed from 10 μA to 1 μA during the run. The measured ^{37}Cl^{5+} currents in the 10 μA range were up to 10% lower than in the 1 μA range. This discrepancy to the measurements with the picoampere source described in Section 2.4 is yet not understood and needs further investigation. For the data from ASTER, the first 10 blocks of each run (~2 min) were excluded because the elimination of the first

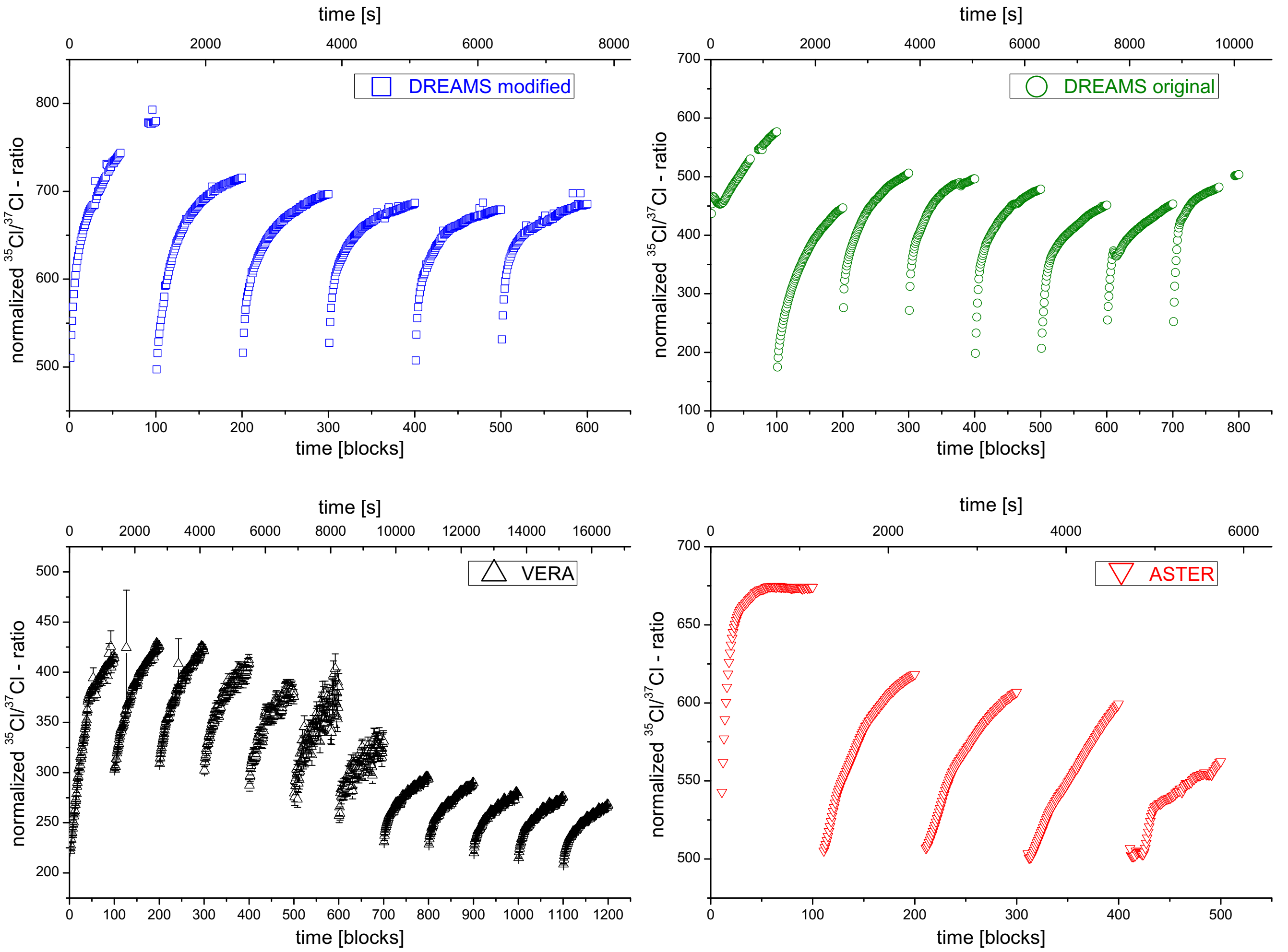

Fig. 2. Normalized ^{35}Cl/^{37}Cl-ratios measured on the sample enriched in ^{35}Cl. Only the values of the blocks that were considered in the data evaluation as described in Sections 3.1 and 3.2 are plotted in the graphs.

2 min of a measurement is a usual procedure set at this facility to reduce the influence of short-time cross-contamination.

Due to fractionation effects in the ion source, during the beam transport and during the stripping process in the accelerator, the measured isotope ratios differ from the nominal ratios in a sample. This fractionation effects most likely induce the scattering of the ^{35}Cl/^{37}Cl-ratios measured during the individual turns listed in Table 2. Therefore, the ^{35}Cl/^{37}Cl-ratio of each block measured on the enriched sample was normalized by the ratio of the theoretical natural ^{35}Cl/^{37}Cl-ratio to the weighted mean of the ^{35}Cl/^{37}Cl-ratios measured on the following samples with natural isotopic composition. The weighted mean was calculated using the uncertainties of the ^{35}Cl/^{37}Cl-ratios calculated from the measurements on each target as weight. At DREAMS in all but one case all four measured samples with natural isotopic composition were used for the normalization. The last measurement on the enriched sample in the modified DREAMS ion source was normalized only to the following three samples with natural isotopic composition, because the measurement had to be aborted due to problems with the electrical stability of the ion source. At ASTER one of the natural chlorine samples was excluded for the normalization because it behaved unstable in the ion source and gave ^{35,37}Cl^{5+} currents, which were a factor of two lower than for the other samples. The weighted mean values of the measured ^{35}Cl/^{37}Cl-ratio are summarized in Table 2. The given uncertainty is the standard deviation of the mean. In most cases, changes of these weighted mean values from turn to turn for the measurements at both DREAMS ion sources are smaller than 1%, indicating that the measurements were reproducible. At ASTER the changes from turn to turn are between 0.7% and 3.3% and the standard deviations of the mean values are >1% indicating that the measurements were not carried out under stable machine conditions. Probably, the explanation is that the tuning was performed with AgCl-samples that were not dry enough, resulting into the explosion of some of the samples. This caused

Table 2
Weighted mean values of the measured ^{35}Cl/^{37}Cl-ratios on samples with natural isotopic composition.

Turn	Modified DREAMS	Original DREAMS	ASTER	VERA
1	3.499 ± 0.009	3.258 ± 0.015	3.71 ± 0.05	3.449 ± 0.008
2	3.5002 ± 0.0040	3.432 ± 0.022	3.59 ± 0.05	3.464 ± 0.009
3	3.4982 ± 0.0042	3.434 ± 0.016	3.540 ± 0.045	3.516 ± 0.019
4	3.500 ± 0.006	3.440 ± 0.011	3.517 ± 0.041	3.596 ± 0.036
5	3.5386 ± 0.0036	3.4412 ± 0.0010	3.490 ± 0.036	3.69 ± 0.07
6	3.514 ± 0.016	3.538 ± 0.006	–	3.81 ± 0.08
7	–	3.5443 ± 0.0046	–	4.15 ± 0.08
8	–	3.550 ± 0.010	–	3.631 ± 0.004
9	–	–	–	3.638 ± 0.005
10	–	–	–	3.642 ± 0.006
11	–	–	–	3.639 ± 0.008
12	–	–	–	3.639 ± 0.008

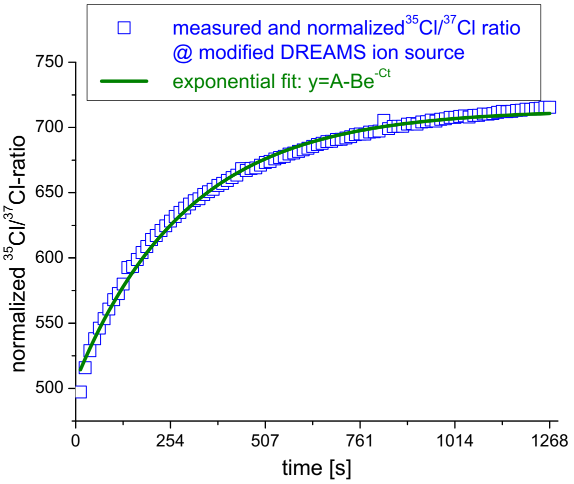

Fig. 3. Exponential fit of the data measured in the second run on the enriched target with the modified DREAMS ion source. The data is normalized as explained in Section 3.1.

Table 3
Saturation values A for the ^{35}Cl/^{37}Cl-ratio of the ^{35}Cl enriched samples in all measurements in all four ion sources. The fit function was not applicable on the first turn measured in the original DREAMS ion source, because it did not converge.

Turn	Modified DREAMS	Original DREAMS	ASTER	VERA
1	781.4 ± 4.9	No fit	674 ± 10	427.9 ± 2.7
2	713.6 ± 1.1	469.8 ± 3.7	635 ± 9	441.0 ± 4.7
3	694.4 ± 1.6	511.4 ± 3.1	629 ± 8	440.7 ± 3.7
4	681.5 ± 1.6	494.7 ± 2.2	750 ± 15	412.2 ± 4.7
5	674.9 ± 1.3	467.9 ± 2.3	568 ± 6	390 ± 8
6	679.2 ± 3.4	439.6 ± 2.2	–	398 ± 15
7	–	451.2 ± 3.7	–	339 ± 10
8	–	476.5 ± 2.3	–	301.0 ± 1.6
9	–	–	–	295.4 ± 1.7
10	–	–	–	282.1 ± 1.3
11	–	–	–	276.3 ± 1.2
12	–	–	–	269.5 ± 1.0

unstable ion source conditions and a tuning which was not optimal.

The normalized ratios of the enriched sample were fitted using the function given in Eq(1), according to a similar model for exponential recovery of an ion source from contamination given in Finkel et al. [19]:

$$y = A - Be^{-Ct} \tag{1}$$

where y is the normalized ^{35}Cl/^{37}C-ratio, A (saturation value), B (defines offset together with A) and C (inverse time constant for ion source recovery) are fit parameters and t is the time. The fit of the second run on the enriched sample measured with the modified DREAMS ion source is shown in Fig. 3. As the samples at ASTER are optimized to give stable ion currents for ~1 h the quality of the data measured in the fourth and especially fifth measurement on the enriched sample is probably suffering from depleted sample material.

3.2. Data evaluation VERA

For the evaluation of the measured data at VERA, the mean value and the standard deviation of the measured ^{35}Cl/^{37}Cl-ratios of 55 cycles (~12.21 s life-time) of the enriched target and 59 cycles (~12.25 s life-time) of the samples with natural ratio were calculated to gain a time structure similar to that of the other two facilities. This could be done for the raw data of all 12 turns measured at VERA. In this process, filter conditions were set to all three measured currents (^{35}Cl^{-}, ^{35}Cl^{7+}, ^{37}Cl^{7+}) and cycles with currents below 10% of the average current over all measurements of the same kind of sample were rejected. Due to this "manual" compression of the data, it is possible to calculate a standard deviation of the ^{35}Cl/^{37}Cl-ratios for every block. This is not possible for ASTER and DREAMS were the measurement intervals of ~12 ms are automatically summarized in blocks by the data acquisition software.

The large changes in the weighted mean values of the measured ^{35}Cl/^{37}Cl-ratios for samples with natural isotopic composition between the turns 4 and 7 at VERA (see Table 2) are due to a damaged stripper foil. In the middle of the 7th turn the stripper foil was replaced. To compensate for the broken foil and the change of the foil, the runs 4–7 on the enriched target were normalized to the two natural samples measured before and afterwards. The last measurement of the enriched sample was normalized to the four natural samples measured before this one. This was done because the measurement sequence ended after the twelfth measurement of the enriched sample. All other measurements of the enriched targets were normalized in the same way as the samples at ASTER and DREAMS. The further data evaluation of the measurements at VERA was the same as at ASTER and DREAMS.

3.3. Results

The results for the fit parameters A, and C are summarized in Table 3 and Fig. 4. The uncertainties for parameter A are calculated from the uncertainty of the fit and the uncertainty from the normalization. The uncertainty for C is not affected by the systematic uncertainty of the normalization. Parameter A, the saturation value, which shows a decreasing trend in all four ion sources, can be used as a measure for the level of contamination with Cl of natural composition in the ion source. From this value, considering the natural ^{35}Cl/^{37}Cl-ratio ($r_{nat} = 3.127$) and the ^{35}Cl/^{37}Cl-ratio of the enriched material ($r_{enr} = 999$), the percentage q of contamination originating from deposited Cl of natural isotopic ratio in the ion source during the sputtering of the targets with natural isotopic composition but also from target preparation and handling, can be calculated using:

$$q = [1 - [(A - r_{nat})(r_{enr} + 1)]/[(A + 1)(r_{enr} - r_{nat})]] \times 100 \tag{2}$$

The individual calculated values for q are presented in Fig. 5.

In the model, parameter C is the inverse time constant for the recovery of the ion source from contamination. In this work the recovery time t_{rec} of the ion source from contamination is defined as:

$$t_{rec} = \ln 2/C \tag{3}$$

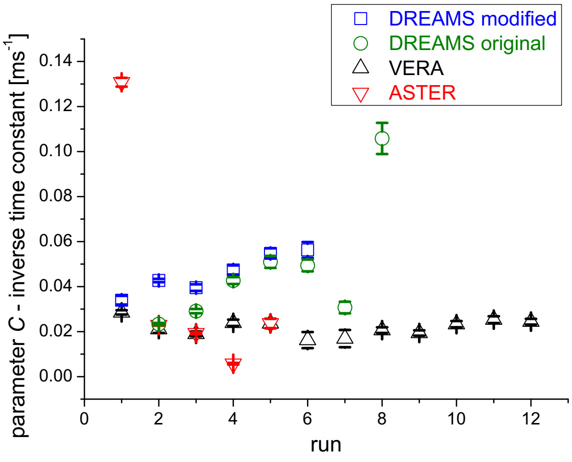

Fig. 4. Inverse time constants C for all measurements in all four ion sources.

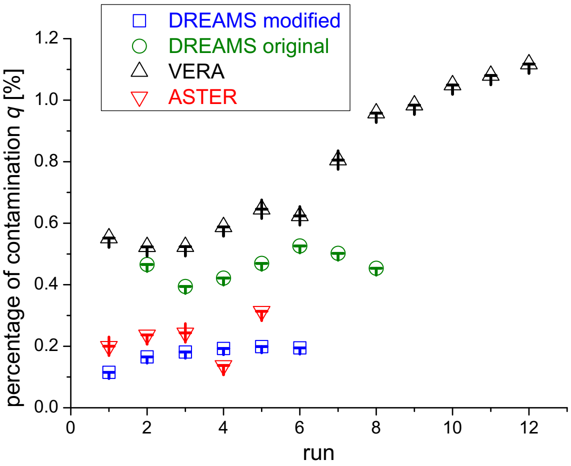

Fig. 5. Percentage of contamination q with Cl of natural isotopic composition in the ion source, while sputtering ^{35}Cl-enriched targets.

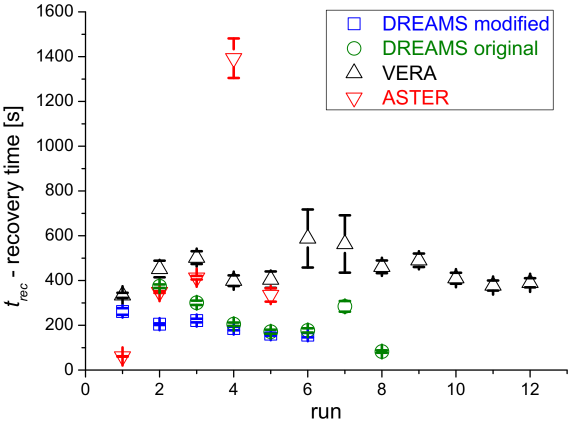

Fig. 6. Recovery times t_{rec} for all measurements in all four ion sources.

Table 4
Recovery times t_{rec} in s for all ion sources in all measurements.

Turn	Modified DREAMS	Original DREAMS	ASTER	VERA
1	262 ± 15	No fit	60.9 ± 0.9	334 ± 11
2	204.9 ± 3.5	375 ± 8	348.1 ± 4.1	451 ± 37
3	221 ± 8	301 ± 10	413 ± 8	502 ± 29
4	186 ± 8	205 ± 7	1390 ± 90	399 ± 24
5	161 ± 7	171 ± 9	335 ± 30	404 ± 37
6	156 ± 10	177 ± 9	–	590 ± 130
7	–	285 ± 24	–	560 ± 130
8	–	83 ± 5	–	461 ± 28
9	–	–	–	490 ± 30
10	–	–	–	410 ± 25
11	–	–	–	378 ± 23
12	–	–	–	390 ± 20

The results for t_{rec} are summarized in Fig. 6 and Table 4. Due to the scatter of the individual values (see Table 4) no average recovery time was calculated.

The uncertainties for q and C were calculated from the uncertainties of the involved parameters A and C.

4. Conclusion

The interlaboratory measurements have shown that all participating ion sources suffer from the long-term memory effect. Whereas the initial contamination, the difference between r_{enr} (^{35}Cl-enriched sample ratio) and A (saturation value) measured in the first run of each ion source is partially caused by different tuning periods with natural Cl samples (see Table 1) different target preparation and also different target holder material, the further decrease of the saturation value can be explained by contamination due to the long-term memory of the ion source. Another possible explanation like time-dependent fractionation, as suggested by Finkel et al. [19], is unlikely considering the performed normalization. According to the measurement procedure and the assumed model during the sputtering of an enriched sample, from turn to turn a generally growing percentage of the sputtered Cl most likely originates from contamination of the ion source with Cl of natural isotopic composition due to the long-term memory effect.

The recovery times of the ion source are widely spread between 61–1390 s at ASTER, and 83–590 s for the other sources. This is in contradiction with the earlier results at ASTER presented in [19]. However, the earlier measurements had a different time structure. The individual samples were sputtered for shorter time periods of about 5 min instead of 21 min for the ^{35}Cl- enriched samples and 4 × 21 min for the samples with natural ratio in this study. The nearly twenty-times longer measurement duration of the samples with natural composition can result in a significantly higher level of contamination. Unfortunately, measurements at ASTER for this work were probably not performed under the best conditions as there were large deviations (see standard deviations in Table 2) in the measurement of the natural Cl ratio, which are explained in Section 3.1. The first run on the enriched target at ASTER is also clearly different from the other runs. The reason for this behavior is not yet understood.

The modified DREAMS ion source shows the highest saturation values, which corresponds to the lowest contamination. Due to the large deviation of the ion source recovery times, no firm conclusion can be given, but in five of six cases the modified DREAMS ion source shows the shortest recovery time (Fig. 6).

5. Outlook

^{35}Cl/^{37}Cl measurements at different AMS-facilities were performed under standard conditions for the particular facility and ion source. Hence, ion source parameters like Cs-temperature, ionizer power and applied voltages differ for all four ion sources, resulting in different currents. For further studies of the integrative effect of the long-term memory, parameters like the amount of vaporized sample material and the efficiency of production of negative Cl, which are hardly accessible with the necessary precision, should be taken into account. One can get a first idea of the integrative effect of the long-term memory by comparing the contamination level to the integrated Cl-currents (see average ^{35}Cl particle current on samples with natural ratio in Table 1) from the samples with natural ratio, on the high-energy side. The original DREAMS ion source clearly shows the highest value here, despite using a higher ionizer power and caesium temperature in the measurements with the modified ion source (see Table 1). As the Cs-temperature and the ionizer power are only indirect parameters to control the amount of Cs and Cs^{+} in the ion source, this may indicate that the emittance or the ionization efficiency of the modified ion source can be improved.

For the prototype of a low long-term memory effect ion source, the modified DREAMS ion source works satisfactorily. In the future, special effort will be given into improving the electrical stability of the ion source. A further possibility to minimize the long-term memory effect and recovery times by installing a cold trap will be investigated.

Due to the fact that all tested ion sources show long-term contamination in the permil to percent range, special precautions should be taken in the measurement of chlorine and iodine samples with ratios spread over more than two orders of magnitude. For isotope dilution AMS, it should also be avoided to use spike material which results in samples with ^{35}Cl/^{37}Cl-ratios spread over more than two orders of magnitude, not only for reasons of current measurement sensitivities as stated in [17] but also to reduce contamination through the long-term memory effect.

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