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Chlorine measurements at the 5MV French AMS national facility ASTER: Associated external uncertainties and comparability with the 6MV DREAMS facility

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ABSTRACT

After 6 years of ^{36}Cl routine operation, more than 6000 unknown samples have been measured at the 5MV French accelerator mass spectrometry (AMS) national facility ASTER (CEREGE, Aix en Provence). This paper presents the long term behavior of ASTER through the analysis of the measurements of the most used chlorine standards and reference materials, KNSTD1600, SM-Cl-12 and SM-CL-13 over a 46 months' time period.

Comparison of measured chlorine concentrations (both ^{35}Cl and ^{36}Cl) from ice samples on two AMS facilities operating at 5MV (ASTER) and 6MV (DREAMS, Helmholtz-Zentrum Dresden-Rossendorf) and normalizing to two different reference materials agree within uncertainties making both reference materials (SM-Cl-12 and KNSTD1600) suitable for ^{36}Cl measurement at ASTER.

1. Introduction

In April 2017, ASTER, the 5MV French Accelerator Mass Spectrometry (AMS) national facility hosted by CEREGE in Aix-en-Provence will pass a decade since the acceptance tests. Since then, ASTER is routinely measuring ^{10}Be and ^{26}Al [1,2]. The ions extracted from a SO110 hybrid ion source [3]are first energy-analysed by a 54 degree electrostatic deflector before being mass-analyzed by a 90 degree magnet equipped with a fast bouncing system that sequentially injects the isotopes of interest with a repetition rate of ~ 100 Hz. A fast beam blanking unit defines with nanosecond resolution the exact duration during which the different isotopes are injected through the accelerator. The HVE model 4150 Tandetron TM accelerator [4] is equipped with an all-solid-state power supply. The high energy-spectrometer features a 90 degree analyzing magnet with Faraday cups installed for measurement of the stable isotopes. Faraday cups are followed by SiN absorber foil and a 35 degree electrostatic deflector. Two sets of Q-pole doublets just before and after the electrostatic deflector serve for proper focusing of the beam that suffers from substantially emittance growth by scattering in the foil. A 30 degree magnet reduces background from ions that have been scattered on the deflector electrodes. The magnet is mounted vertically to uncouple the dispersive action of the electrostatic deflector and the magnet. The measurement of all isotopes is gated in synchronization with their corresponding injection periods. The rare isotope is detected in a high-resolution, 4-anode gas ionization chamber.

Because regarding volatile elements (^{36}Cl, ^{129}I) the initial Cs-sputter ion source SO110 induced sample-to-sample cross-contamination, the source and aperture designs as well as the shape of the cathodes have been upgraded to reduce the resulting memory effects to significantly less than ~0.1%, allowing routine measurements of these volatile elements [5,6] since 2010. More specifically, an average number of 1000 ^{36}Cl unknown targets are measured per year, all being normalized to AgCl materials (KNSTD1600; $^{36}\mathrm{Cl}/^{35}\mathrm{Cl} = 2.112 \times 10^{-12}$) prepared by Kuni Nishiizumi [7]. To monitor the long term variability of ASTER and to determine the external uncertainties associated to the $^{36}\mathrm{Cl}/^{35}\mathrm{Cl}$, $^{36}\mathrm{Cl}/^{37}\mathrm{Cl}$ and $^{35}\mathrm{Cl}/^{37}\mathrm{Cl}$ ratios, it has be decided to measure together with the KNSTD1600 standard, the SM-Cl-X reference materials. Prepared by S. Merchel under the auspice of the European project "CRONUS-EU", these SM-Cl-X reference materials have been cross-calibrated through an interlaboratory comparison involving eight AMS facilities worldwide. The resulting round-robin data are fully presented in Merchel et al. (2011) [8]. The aim of this paper is therefore not to refine the SM-Cl-X standards calibration with more data points but to

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Table 1
Typical specifications for chlorine measurements at ASTER and at DREAMS AMS (modified from [1] to [9]). Both facilities use a modified HVE source SO110.

	Extraction as	^{35}Cl currents (μA)	Terminal Voltage (MV)	Charge state after gaz stripper	Charge state after absorber foil	Background (10^{-15})
ASTER	Cl^- at 29.5 kV	15–25	5	5^+	10^+	0.28
DREAMS	Cl^- at 25 kV	20–30	6	5^+	11^+	0.4

quantify the external uncertainties associated to chlorine measurements at the 5MV French Accelerator Mass Spectrometry (AMS) national facility ASTER. These measurements also aimed at replacing the KNSTD1600 standard whose availability is not guaranteed in the long term, by the SM-Cl-X reference materials. In order to confirm the change of reference material after a 46-month period of measurements of SM-Cl-X vs. KNSTD1600 at ASTER, an inter comparison has been conducted on an identical batch of samples measured ^{36}Cl concentrations measured in the same ice samples both at ASTERand at DREAMS, the 6MV AMS-facility hosted by the HDZR Ion Beam Center in Dresden [9,10,11] (Table 1)are then compared for these two AMS facilities working at different energies and provide results normalized to different standards (KNSTD1600 for ASTER, SMCl-XX for DREAMS. For this inter comparison, modern snow samples from Antarctica have been chosen for their high ^{36}Cl content and their low natural chlorine concentration on the order of 100 ppb. In addition to compare the ^{36}Cl/^{35}Cl and the ^{36}Cl/^{37}Cl ratios given by the two AMS facilities along with the calculated ^{36}Cl concentration, the natural chlorine concentration has been determined by isotopic dilution and compared to the values independently obtained by ion chromatography.

2. Determination of the external uncertainties

2.1. Chlorine measurements at ASTER

At ASTER, chlorine measurements are performed as explained hereafter:

Standardization

- 3 or 4 cathodes of KNSTD1600 standard are measured per batch. Each cathode is measured three times 10 min divided in 20 blocks of 30 s each. The first 2 min of each measurement period are discarded since they may potentially be affected by memory effects. Typical ^{35}Cl currents are ranging from 25 to 30 μA and regarding ^{36}Cl, 7.000–15.000 events are detected.
- At the end of the batch, the three individual measurements performed on each KNSTD1600 cathode are statistically compared (using a Chi2 test following [12]) and recombined to provide the measured ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl ratios associated to each KNSTD1600 cathode. Considering then the 3 to 4 different KNSTD1600 standard cathodes, their respective ratios are compared following the same Chi2 test and a weighted mean is calculated that allows determining the machine response and the correction factor to apply to back calculate the ratios associated to the samples to be measured (three corrections factors are thus determined, one for ^{36}Cl/^{35}Cl, one for ^{36}Cl/^{37}Cl, and one for ^{35}Cl/^{37}Cl).

Unknown measurements

- Samples are measured three times 20 min divided in 40 blocks of 30 s each. Similarly, the first 2 min of each measurement period are discarded and the three measurements (20 min each) are compared and recombined to provide ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl ratios that are finally multiplied by the previously determined correction factors to obtain the sample ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl ratios. The previously described procedure is the procedure by default used for the majority of the samples. Highly ^{36}Cl concentrated samples implying a significantly higher counting statistics may only be measured three times 5 min divided in 15 blocks of 20 s each.

Together with standards and unknown samples, one background cathode filled with a natural chlorine carrier with a low ^{36}Cl content is measured to monitor the cleanliness of the ion source (^{36}Cl/^{35}Cl $< 3.10^{-15}$)

2.2. External uncertainties determination

From February 2013 to December 2016, SM-Cl-12 and SM-Cl-13 reference materials were measured together with the KNSTD1600 standard. As the internationally cross-calibrated SM-Cl-12 reference material may eventually be considered as a substitute for KNSTD1600, an equivalent number of SM-Cl-12 and KNSTD1600 cathodes were measured. In addition, one SM-Cl-13 cathode was measured per batch as SM-Cl-13 will be used to monitor the long term stability of ASTER. Over the covered time period, this represents 189 cathodes of SM-Cl-12 and 31 cathodes of SM-Cl-13 measured.

Assuming a Gaussian distribution centered on the mean, cumulative distribution functions ordering the measurements from the minimum to the maximum value have been plotted for the SM-Cl-12/KNSTD1600 (Fig. 1) and the SM-Cl-13/KNSTD1600 (Fig. 2) ratios considering all ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl individual measurements. All ratio measurements (SM-Cl-12/KNSTD1600 and SM-Cl-13/KNSTD1600) are presented in the Supplementary Material (Sup Table 1).

The distribution function used is F(x,μ,sigma) = $\frac{1}{\sqrt{2\pi\sigma}}e^{\left[\frac{(x-\mu)^2}{(2\sigma)^2}\right]}$ where x is the ratio (^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl or ^{35}Cl/^{37}Cl) for which we are looking for the distribution; μ, the mean; and , the standard deviation. The mean standard error is calculated as follows: mean standard error = $\sqrt{\left[\frac{stand.dev.}{\sqrt{Numberofmeasur.}}\right]^2}$ (Table 2). When all SM-Cl –X/KNSTD1600 ratios for each isotopic ratio (^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl) are taken into account, they do not satisfy the Chi2 test for none of the three ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl ratios (Table 2).

To make all these isotopic ratios satisfy the Chi2 test, an external machine error has thus to be added to the analytical uncertainties (counting statistics + variability of the standard during the batch). Contrary to ^{10}Be and ^{9}Be, yielding to one isotopic ratio and thus to one external machine error, this has to be done in the peculiar case of chlorine for the three isotopic species yielding to 3 isotopic ratios. For SM-Cl-12, all SM-Cl-12/KNSTD1600 ratios belong to the same population for a given isotopic ratio providing that an external uncertainty of 2.74%, 2.13% and 1.62% is added to the analytical uncertainties for ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl ratios, respectively. Regarding SM-Cl-13, all SM-Cl-13/KNSTD1600 ratios belong to the same population for a given isotopic ratio providing that an external uncertainty of 2.06%, 2.31% and 1.58% is added to the analytical uncertainties for ^{36}Cl/^{35}Cl, ^{36}Cl/^{37}Cl and ^{35}Cl/^{37}Cl ratios, respectively (Table 3 and 4).

To our knowledge, the determined external uncertainties presented above are the first one reported for an AMS facility working at such low ion energy (~30 MeV) and using a post stripping degrader foil. They are in agreement with those presented by the SUERC group using a different AMS technology but working at the same energy. SUERC group has proposed uncertainties of ~3% and 1.5% for ^{36}Cl/Cl ratios