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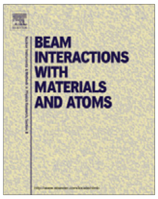

Recent advances in AMS of ^{36}Cl with a 3-MV-tandem

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ABSTRACT

Accelerator mass spectrometry (AMS) of ^{36}Cl ($t_{1/2}$ = 0.30 Ma) at natural isotopic concentrations requires high particle energies for the separation from the stable isobar ^{36}S and was so far the exclusive domain of tandem accelerators with at least 5 MV terminal voltage. Using terminal foil stripping and a detection setup consisting of a split-anode ionization chamber and an additional energy signal from a silicon strip detector, a ^{36}S suppression of >10^4 at 3 MV terminal voltage was achieved. To further increase the ^{36}S suppression energy loss straggling in various counter gases (C_4H_{10}, Ar–CH_4 and C_4H_{10}–Ar) and the effect of "energy focusing" below the maximum of the Bragg curve was investigated. The comparison of experimental data with simulations and published data yielded interesting insights into the physics underlying the detectors. Energy loss, energy straggling and angular scattering determine the ^{36}S suppression. In addition, we improved ion source conditions, target backing materials and the cathode design with respect to sulfur output and cross contamination. These changes allow higher currents during measurement (^{35}Cl$^-$ current ≈ 5 μA) and also increased the reproducibility. An injector to detector efficiency for ^{36}Cl ions of 8% (16% stripping yield for the 7+ charge state in the accelerator, 50% ^{36}Cl detection efficiency) was achieved, which can favorably be compared to other facilities. The memory effect in our ion source was also thoroughly investigated. Currently our measured blank value is ^{36}Cl/Cl ≈ 3×10^{-15} when samples with a ratio of 10^{-11} are used in the same sample wheel and ^{36}Cl/Cl ≈ 5×10^{-16} if measured together with samples with a ratio of 10^{-12} or below. This is in good agreement with the lowest so far published isotope ratios around 5×10^{-16} and demonstrates that 3 MV tandems can achieve the same sensitivity for ^{36}Cl as larger machines.

1. Introduction

Medium-sized tandem-accelerators are capable to measure all AMS-isotopes where no stable isobars interfere [1]. Isobar suppression based on the different energy loss in matter has been established already in the early days of AMS (see e.g. [2–4]), but only facilities with 5 MV or more terminal voltage could provide sufficient energy to extend efficient isobar separation into the mass region of ^{36}Cl. At VERA (Vienna Environmental Research Accelerator) we have performed the first ^{36}Cl exposure dating measurement with a 3 MV tandem accelerator, operating our machine at 3.5 MV, using foil stripping and a split-anode ionization chamber [5]. In a different work, we evaluated the performance of various detectors for ^{36}Cl in order to achieve similar ^{36}S suppression already at lower terminal voltage [6]. While these measurements yielded first promising results, considerable effort was necessary to allow routine measurements of ^{36}Cl at 3.0 MV terminal voltage. This paper describes these advances including our investigations of the detection system regarding energy loss and energy straggling in various detector gases and the behavior of the ion source.

2. Detection setup and ^{36}S suppression

Fig. 1 shows a schematic diagram of our current detector setup. It consists of a split-anode ionization chamber based on a design developed at the ETH Zurich [7], with 5 × 5 mm silicon nitride entrance and exit windows ([8], 100 nm thickness from Silson Ltd., UK) followed by a double-sided silicon strip detector (Micron Semiconductors Design W1, 50 × 50 mm active area, 256 pixels) sitting 30 cm behind the exit window of the ionization chamber. The best separation was achieved by adjusting the detector gas pressure such, that the ions have lost ~5/6 of their initial energy when leaving the ionization chamber. The actual ^{36}S suppression depends strongly on the acceptance of the ^{36}Cl gates and thus on

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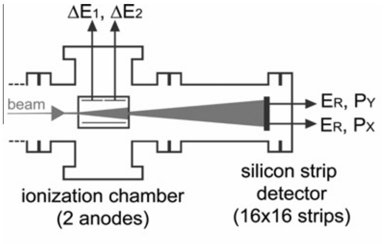

Fig. 1. Schematic of our current detection system for ^{36}Cl providing two independent energy loss measurements (ΔE_1, ΔE_2), two residual energy measurements (E_R) and X/Y position information (P_X, P_Y).

the ^{36}Cl detection efficiency. All ^{36}S suppression values in this paper are for 50% ^{36}Cl detection efficiency, including losses caused by angular straggling in the detector system. The ^{36}S suppression factors are determined using an attenuated beam from a stainless steel sample (blank) as the ratio of events in the $^{36}S^{7+}$ peak versus the number of events in the $^{36}Cl^{7+}$ integration bin, multiplied by the ^{36}Cl acceptance of the detection system (0.5). Process blanks made of ^{36}Cl free chlorine material from, e.g., rock salt are less suitable for this purpose, since their ^{36}S count rates are usually to low to acquire sufficient statistics.

With the ionization chamber alone, the achieved ^{36}S suppression at 3.5 MV terminal voltage (28 MeV particle energy) was 30,000 [5]. However, the suppression drops to a mere 1600 at 3 MV (24 MeV particle energy) [6]. With an additional residual energy signal from a silicon strip detector, ^{36}S suppression factors above 10,000 at 3 MV were obtained. This considerable increase is mainly due to the fact that unwanted high energy tails in the ionization chamber spectra arising from angular scattering are suppressed by accepting only events in coincidence with the strip detector. The resulting spectra are purely Gaussian shaped peaks over several orders of magnitude (Fig. 2). As scattered ions have a longer flight path through the chamber and subsequently deposit more of their kinetic energy and also the recoil particles lead to additional ionization, some scattered ^{36}S ions would end up in the ^{36}Cl bin. However, ions with inclined flight paths usually do not pass the exit window aperture of the ionization chamber and are rejected. It should be noted that the experimental data including the scattering tails can be well reproduced by using the TRANSMIT-files, which are generated by the computer code SRIM [9], as shown in Fig. 2. Unfortunately, it turned out that the position information from the silicon strip detector gives no additional information on the flight path through the ionization chamber as it mostly depends on the scattering angle in the exit foil.

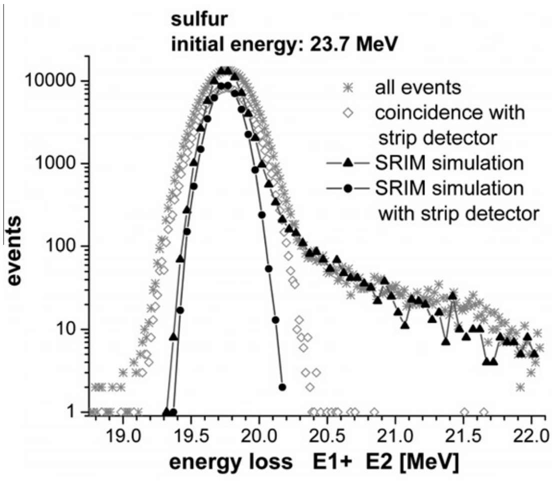

Fig. 2. Comparison of experimental total energy loss spectra from the ionization chamber with a SRIM simulation. Note that the energy tails, which are caused by scattering events (nuclear stopping) are well reproduced in the SRIM simulation, whereas the inner part of the peak, which can be well described with a normal distribution, is predominantly caused by straggling of the electronic stopping process, which is underestimated in the simulation. This is in agreement with the energy straggling obtained in the model of Yang [10]. The initial energy of 23.7 MeV instead of 24.07 MeV compensates already for the energy loss in the entrance window.

3. ^{36}S suppression in various detector gases

Motivated by a work from Schmidt-Böcking and Hornung [11], we studied various detector gases (argon–methane, isobutane, isobutane–argon) with respect to the parameters determining the ^{36}S suppression: energy loss straggling (peak width), separation between Cl and S peaks and transmission through the detector (angular scattering). As illustrated in Fig. 3, the effect of energy focusing [12] occurring below the maximum of the Bragg curve has a strong influence on the peak widths. Due to the decrease of stopping power with decreasing energy, ions that have already lost more energy than the average ion are likely to deposit less energy than average in the following part of the detector, resulting in a decrease in energy spread. Up to energy losses of ~15 MeV, argon + 10% methane as detector gas gives ~10–15% lower energy straggling and better peak separation compared to isobutane. Simulations based on the straggling formula given in [11] using the energy loss data from Northcliffe and Schilling [13] reproduce this trend, although the experimental data with argon–methane for large energy losses ($\Delta E > 18$ MeV) deviate from simulations and lead to a larger straggling than in isobutane. A reason might be, that Ar has a higher nuclear stopping, which increases the energy straggling at lower residual energies (this effect is not considered in the simulations). Sample spectra are shown in Fig. 4. On the other hand, due to the lower stopping power of argon–methane, a higher gas pressure of 150 mbar had to be used instead of 45 mbar for C_4H_{10}. Together with the higher angular scattering cross section of argon, this resulted in a transmission of only 59% through the ionization chamber compared to 90% for isobutane. Since the ^{36}Cl bin size had to be chosen accordingly for 50% Cl detection efficiency, we achieved a ^{36}S suppression of only ~3000 for argon–methane and ~11,000 for isobutane respectively. A mix of the two gases (isobutane with 30% argon, 65 mbar) seems the best compromise between good peak separation and high transmission and yielded a ^{36}S suppression of 20,000.

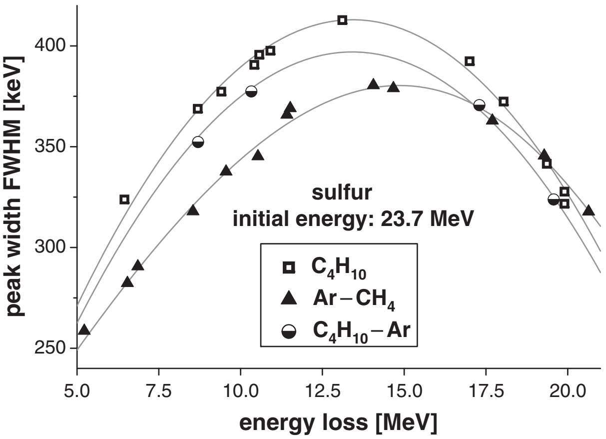

Fig. 3. Energy loss straggling of ^{36}S with an initial energy of 23.7 MeV in various counter gases. The energy focusing effect at the end of the energy loss curve is clearly apparent.

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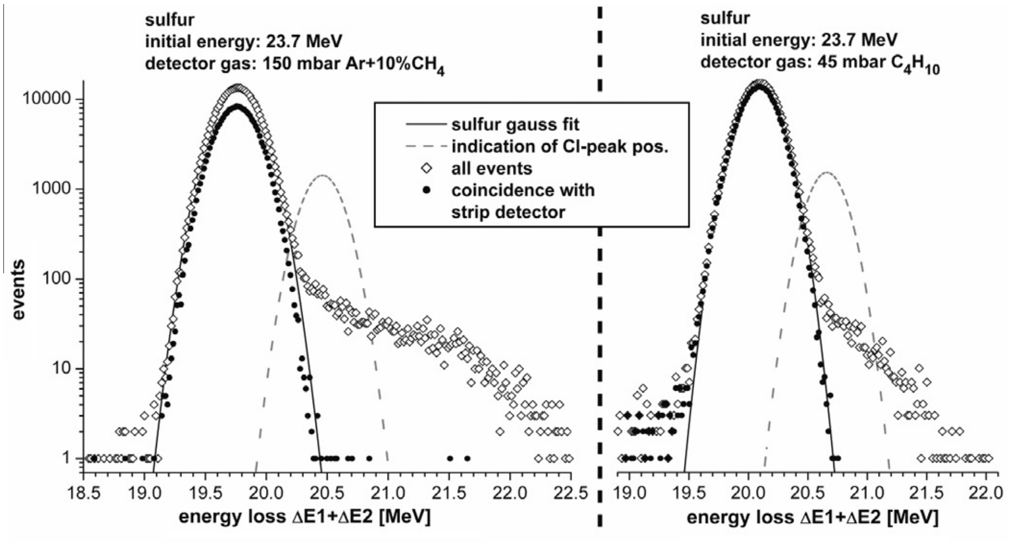

Fig. 4. Comparison of sulfur energy loss spectra recorded on a steel target with the ionization chamber filled with isobutane and argon–methane respectively. The Cl-peak position was determined in different runs on a standard material with ^{36}Cl/Cl = 10^{-11}. Despite better peak separation, Ar$-$CH$_4$ does not provide higher ^{36}S suppression because of the pronounced angular scattering tail.

4. Sulfur and chlorine output from the ion source

Since the sulfur count rate in the detector is the limiting factor for the beam current, it was crucial to reduce the sulfur output from our SNICS ion source. Earlier experiments have shown, that the sulfur content of the silver chloride itself is very low [5] and most of the sulfur comes from the surrounding sample holder and backing materials. Therefore, we are now using cylindrical Cu-cathodes (6 mm diameter) with a conical hole (5 mm inner diameter) coated with silver bromide as backing material. A new sample wheel design allows loading 40 cathodes, which are held by clips on the backside of the wheel. We screened different batches of commercially available AgBr but achieved the best results with our own AgBr produced at the VERA laboratory from KBr cleaned from sulfur by precipitation of BaSO$_4$. We also tried tantalum plates as backing material, but despite etching with hydrofluoric acid and/or baking in H$_2$ for several hours at 700 °C the sulfur output was still one order of magnitude higher than from AgBr. Experiments with Ni-cathodes (without additional backing material) yielded similar results.

To achieve constant output from our Cs-sputter source, we use the current from the source high voltage power supply for a feedback regulation of the ionizer power, while the cesium oven temperature is kept constant at typical values used for other AMS isotopes. The regulation used has ID (integration–differentiation) characteristics, and achieves the same Cl$^-$ current on all samples in the wheel typically within 100 s after sample change. During the measurement, the Cl$^-$ current can be kept constant within 25%.

During our investigations, we found a strong dependence of the sulfur output on the ionizer power (Fig. 5, obtained actually with an unfavorable set of source regulation parameters that lead to overshoots of the regulation and therefore oscillation of the ionizer power). A 30% change in ionizer power can induce a change in the S$^-$ to Cl$^-$ ratio by a factor of up to 40 (for unknown reasons not further investigated, the Cl$^-$-current was almost constant during this measurement). With optimized parameters of the regulation, the average sulfur output from our ion source is ^{36}S$^-$/^{35}Cl$^-$ $\approx 5 \times 10^{-11}$ corresponding to a detector count rate of ~300 Hz at 5 μA ^{35}Cl$^-$-current and a sulfur induced signal in the ^{36}Cl bin of ^{36}Cl/Cl $\approx 2.5 \times 10^{-15}$.

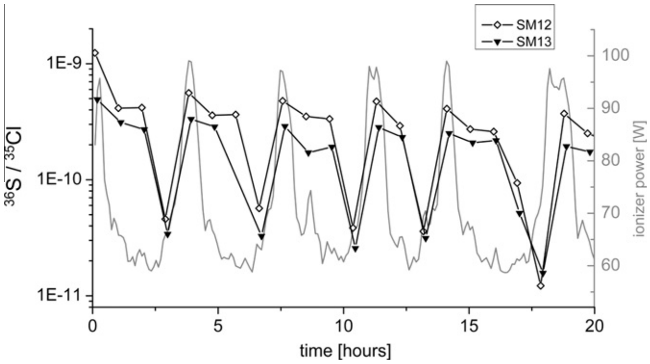

Fig. 5. Sulfur output from two samples (SM12 and SM13) and ionizer power during a 40 h beam time. Each point shows the results from one run lasting ~5 min. The ionizer power was adjusted to keep the ^{35}Cl$^-$ current stable at 1 μA.

5. Cross contamination and memory effect in the ion source

The memory effect of the ion source was studied by periodic measurements on a set of blank samples. The average initial blank value after sulfur induced background correction was ^{36}Cl/Cl $\approx (4 \pm 8) \times 10^{-16}$. In the next step, a 10^{-12} standard material mounted at the opposite side of the sample wheel was sputtered for several minutes at the beginning of each measurement cycle. The observed memory effect of the ion source on the first blank sample was below 10^{-3} and after 30 min no more statistically significant increase of the blank value was observed. When sputtering a 10^{-11} standard, the blank value after sulfur induced background correction starts at ^{36}Cl/Cl $\approx (1.4 \pm 0.2) \times 10^{-14}$ and follows an almost exponential decrease with a time constant of ~60 min to a constant blank value of ^{36}Cl/Cl $\approx (3 \pm 1) \times 10^{-15}$. After 24 h of source "cleaning" on a new blank cathode, a second measurement series only on the blank samples yielded that, independent from the cathode positions, the first blank sputtered after the standard in the cycle still showed the highest cross contamination (^{36}Cl/Cl $\approx (3.0 \pm 0.7) \times 10^{-15}$ compared to ^{36}Cl/Cl $\approx (1.5 \pm 0.5) \times 10^{-15}$ on the last sample in the cycle). In our understanding, Cl vapor from the samples also takes part in the sputtering process and therefore is implanted in the following target materials at a level

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of $\sim 10^{-4}$. Taking these effects into account, their influence can be mitigated by careful choice of the target order and the use of appropriate standard materials.

6. Conclusions and outlook

After correction of any drifts in the energy loss spectra by locking the sulfur peak position, the reproducibility of the ^{36}Cl/Cl isotopic ratio measurements is ~2% for 10^{-12} samples. We achieve an injector to detector efficiency for ^{36}Cl ions of 8% (16% stripping yield for the 7+ charge state in the accelerator, 50% ^{36}Cl detection efficiency), which also compares favorably to other facilities [14–16]. A ^{36}Cl round robin intercomparison of several AMS labs [17] in the early stages of this work yielded that previous deviations of our results from others reported by Steier et al. [5] have been resolved and were mainly due to a wrong nominal value used for the standard material. In the near future, we aim to reduce the amount of AgCl required for a decent measurement (currently ~4 mg AgCl) and some advances have already been made with samples $\leqslant$1 mg AgCl.

Recently, based on the development described in this paper, more measurements on real exposure dating samples in the range of $^{36}\mathrm{Cl/Cl} = 3 \times 10^{-14}$ to 10^{-11} have been successfully performed (results will be published separately). This further demonstrates that measurements competitive to larger tandems are possible at 3 MV terminal voltage.

We hope that our new findings will be helpful not only for 3-MV-tandems but also for larger machines at even higher masses.

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References

[1] P. Steier, R. Golser, V. Liechtenstein, W. Kutschera, A. Priller, C. Vockenhuber, A. Wallner, Nucl. Instr. Meth. Phys. Res. B 240 (2005) 445.
[2] R.A. Muller, Science 196 (1977) 489.
[3] D. Fink, O. Meirav, M. Paul, H. Ernst, W. Henning, W. Kutschera, R. Kaim, A. Kaufman, M. Magaritz, Nucl. Instr. Methods Phys. Res. B 5 (1984) 123.
[4] G. Raisbeck, F. Yiou, D. Bourles, J. Lestringuez, D. Deboffle, Nucl. Instr. Methods Phys. Res. B 5 (1984) 175.
[5] P. Steier, O. Forstner, R. Golser, W. Kutschera, M. Martschini, S. Merchel, T. Orlowski, A. Priller, C. Vockenhuber, A. Wallner, Nucl. Instr. Methods Phys. Res. B 268 (2010) 744.
[6] T. Orlowski, O. Forstner, R. Golser, W. Kutschera, M. Martschini, S. Merchel, A. Priller, P. Steier, C. Vockenhuber, A. Wallner, Nucl. Instr. Methods Phys. Res. B 268 (2010) 847.
[7] M. Stocker, M. Doebeli, M. Grajcar, M. Suter, H.-A. Synal, L. Wacker, Nucl. Instr. Methods Phys. Res. B 240 (2005) 483.
[8] M. Doebeli, C. Kottler, M. Stocker, S. Weinmann, H.-A. Synal, M. Grajcar, M. Suter, Nucl. Instr. Methods Phys. Res. B 219–220 (2004) 415.
[9] J.F. Ziegler, James Ziegler – SRIM & TRIM, <http://www.srim.org/> (accessed 27.10.08).
[10] Q. Yang, D.J. O'Connor, Z. Wang, Nucl. Instr. Methods Phys. Res. B 61 (1991) 149.
[11] H. Schmidt-Böcking, H. Hornung, Z. Physik A286 (1978) 253.
[12] M. Suter, M. Döbeli, M. Grajcar, A. Müller, M. Stocker, G. Sun, H.A. Synal, L. Wacker, Nucl. Instr. Methods Phys. Res. B 259 (2007) 165.
[13] L.C. Northcliffe, R.F. Schilling, Nucl. Data Tabl. A7 (1970) 233.
[14] C. Maden, P.A.F. Anastasi, A. Dougans, S.P.H.T. Freeman, R. Kitchen, G. Klody, C. Schnabel, M. Sundquist, K. Vanner, S. Xu, Nucl. Instr. Methods Phys. Res. B 259 (2007) 131.
[15] H.-A. Synal, J. Beer, G. Bonani, Ch. Lukasczyk, M. Suter, Nucl. Instr. Methods Phys. Res. B 92 (1994) 79.
[16] M.G. Klein, A. Gottdang, D.J.W. Mous, D.L. Bourlès, M. Arnold, B. Hamelin, G. Aumaître, R. Braucher, S. Merchel, F. Chauvet, Nucl. Instr. Methods Phys. Res. B 266 (2008) 1828.
[17] S. Merchel, W. Bremser, V. Alfimov, M. Arnold, G. Aumaître, L. Benedetti, D.L. Bourlès, R. Braucher, M. Caffee, M. Christl, L.K. Fifield, R.C. Finkel, S.P.H.T. Freeman, A. Ruiz-Gómez, P.W. Kubik, D.H. Rood, K. Sasa, P. Steier, S.G. Tims, A. Wallner, K.M. Wilcken, S. Xu, Geochim. Cosmochim. Acta 73/13 (2009) A871.

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