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Light induced suppression of sulfur in a cesium sputter ion source

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ABSTRACT

New techniques for suppression of atomic isobars in negative ion beams are of great interest for accelerator mass spectrometry (AMS). Especially small and medium-sized facilities can significantly extend their measurement capabilities to new interesting isotopes with a technique independent of terminal voltage. In a new approach, the effect of continuous wave laser light directed towards the cathode surface in a cesium sputter ion source of the Middleton type was studied. The laser light induced a significant change in oxygen, sulfur and chlorine negative ion production from a AgCl target. Approximately 100 mW of laser light reduced the sulfur to chlorine ratio by one order of magnitude. The effect was found to depend on laser power and ion source parameters but not on the laser wavelength. The time constant of the effect varied from a few seconds up to several minutes. Experiments were first performed at the ion beam facility GUNILLA at University of Gothenburg with macroscopic amounts of sulfur. The results were then reproduced at the VERA AMS facility with chemically cleaned AgCl targets containing ~1 ppm sulfur. The physical explanation behind the effect is still unclear. Nevertheless, the technique has been successfully applied during a regular AMS measurement of ^{36}Cl.

1. Introduction

The sensitivity of accelerator mass spectrometry (AMS) for a rare nuclide is limited by the ability to distinguish it from abundant neighboring masses and from atomic isobar interferences. Molecular isobars, i.e. molecules with almost the same mass as the ion of interest, can be effectively removed by their break-up in the stripping process of a tandem accelerator. Atomic isobars, i.e. atoms with almost the same mass, but from a nearby element, are more difficult to separate and typically require particle energies around 1 MeV/amu. At these energies isobaric discrimination based on the different energy loss of the ions in matter becomes available. However, usability depends strongly on the available energy and on the relative difference in atomic number. Heavy isobars like ^{53}Mn and ^{53}Cr can be separated only at two of the largest facilities worldwide, that operate at terminal voltages of 14 MV [1,2]. To separate ^{36}Cl and ^{36}S, energies of at least 30 MeV are commonly used. With an optimized detection system, the Vienna Environmental Research Accelerator (VERA) is so far the only 3-MV-AMS facility, where measurements of ^{36}Cl at natural isotopic levels can be performed, that are competitive to larger facilities [3,4].

In fortunate cases, e.g. ^{14}C or ^{26}Al, the stable atomic isobars do not form negative ions and are thus suppressed already in the ion source. The lack of atomic isobars in these ion beams has allowed a lowering of the terminal voltage into the 200 kV range instead of several MV [5].

Therefore, element-selective techniques have been investigated to suppress isobaric interferences in an ion beam prior to injection into the accelerator. We are aware of two promising methods. Recently, a sulfur-to-chlorine suppression factor of at least 10^3 was demonstrated [6] using optical filtering via selective photodetachment in an ion cooler, which increased the interaction time of the ion beam and the laser beam. The other approach using resonant charge transfer in a NO_2-filled gas reaction cell yielded an even higher sulfur suppression of 10^6 [7]. Both methods, however, require substantial modifications of the injection system of existing accelerators to adapt for an ion cooler or a gas cell. Furthermore, total current throughput of both devices is limited to a few nA, which is less than 1‰ of typical ion beam currents in AMS measurements.

In this paper we report on a new technique for ^{36}S–^{36}Cl separation. It does not give comparable high suppression factors but can be readily implemented at most facilities as an additional means for isobar separation. The method is based on optical interaction with the environment immediately in front of, or at the surface of the cathode in a cesium sputter negative ion source of the Middleton type [8]. It requires only a free optical path to the target and a high

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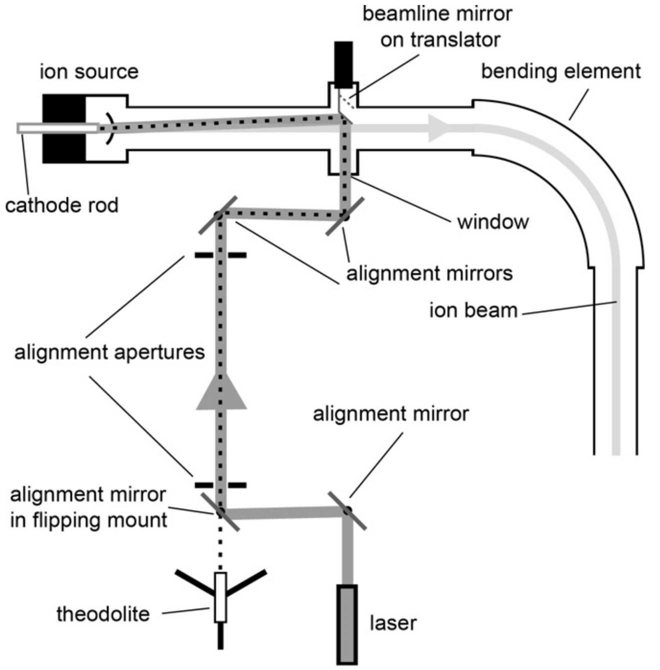

Fig. 1. Schematic of the optical setup used at GUNILLA and VERA.

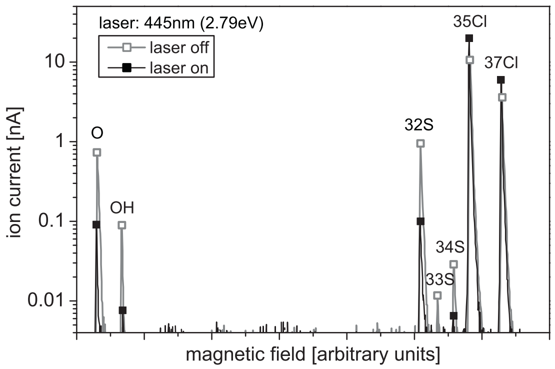

Fig. 2. Mass spectra obtained at GUNILLA by scanning the analyzing magnet. The figure shows the ion currents without laser light and with 100 mW of laser light with a wavelength of 445 nm (2.79 eV).

power laser. Previous experiments with high power pulsed lasers, but different goals in mind [9,10], revealed interesting changes in the sulfur and chlorine production. In AMS measurements of ^{36}Cl, the sulfur suppression by our new technique significantly reduces the ^{36}S count rate in the detector. This is of interest for all facilities where the ion beam is injected into the detection setup without prior sulfur separation [11–13] in order to achieve high efficiency. At VERA, suppression of sulfur by one order of magnitude is sufficient to allow a reduction of the amount of sample material (AgCl) required for a reliable ^{36}Cl measurement [4]. Furthermore, the method is beneficial for measurements of samples with isotopic ratios ^{36}Cl/Cl < 5×10^{-15}.

2. Experimental setup

Experiments were performed at the GUNILLA facility of the University of Gothenburg [14,15] and at VERA at the University of Vienna using a new injector [16]. In both experiments the same 1.2 W, 445 nm continuous wave diode laser was used. The corresponding photon energy of 2.79 eV lies between the electron affinities of sulfur (2.077 eV) and chlorine (3.613 eV) [17]. Thus, sulfur suppression by photodetachment is energetically possible. At GUNILLA, we also investigated the effect of a 1064 nm (1.17 eV) laser with similar output power.

The optical setup was almost identical at both facilities and is shown schematically in Fig. 1. The laser beam entered the ion beamline through a borosilicate window and was directed by a set of four mirrors outside and one mirror inside the vacuum chamber. Two apertures were centered on the laser beam path and positioned about 1 m apart. The mirror placed inside the vacuum chamber was covered by a glass plate with a transparent, conductive layer of ITO (In_2O_3:SnO_2). This prevented the glass plate and the mirror from being charged by stray ions that unavoidably hit the mirror. The outside mirror situated in front of the first aperture was mounted in a flipping mirror mount. By flipping this mirror out of the optical path it was possible to optically observe the cathode and the hot ionizer using a theodolite. The system was aligned such that the cathode appeared centered in the two apertures. This ensured that the laser light hit the cathode when the flipping mirror was inserted in the beam path. Fine tuning of the alignment was achieved by maximizing the effect caused by the laser on either the sulfur or the chlorine signal. The maximum laser power at the cathode position in a 1 mm × 1 mm area was approximately 200 mW at GUNILLA and 400 mW at VERA. The highest losses came from absorption in the ITO coated glass plate (about 20% measured at 445 nm). The optical losses for both wavelengths were about 10% in the borosilicate window and about 5% in each mirror.

At GUNILLA the sample material was AgCl containing approximately 10% AgS. Around 500 mg of this material was pressed into a cylindrical cathode with 5 mm inner diameter. At VERA the samples contained 2–20 mg AgCl pressed into a copper cathode with AgBr backing. The area covered with AgCl was 1–3 mm in diameter. Since VERA is an AMS facility, only microscopic amounts of sulfur could be put into the ion source in order to avoid contamination in future measurements. Most samples contained chemically cleaned AgCl with a typical sulfur content of approximately 1 ppm.

At GUNILLA, only one mass can be measured at a time. Hence, the time structure of the effect had to be studied consecutively for various isotopes. At VERA, on the other hand, several masses can be measured almost simultaneously using offset-Faraday-cups and particle detectors. Here, the switching time between the different detectors allowed for several measurements per second.

3. Results

3.1. Results with macroscopic amounts of sulfur (GUNILLA)

Fig. 2 shows a comparison of two mass spectra recorded with and without laser. An increase in chlorine current by a factor of 2 and a decrease in oxygen and sulfur currents by more than a factor of 5 were observed when approximately 100 mW of laser light was directed onto the cathode. The ion currents did not change immediately after switching the laser on or off. The time constants for the currents to adjust to a change in laser intensity were of the order of several seconds up to minutes. Since we could not resolve atomic from molecular ions, the mass peaks could possibly contain substantial molecular contributions. This is, however, unlikely since the measured isotopic abundances match the natural abundances of sulfur and chlorine isotopes. In particular, there was no observed excess at mass 32, indicating only little if any interference from O_2. After sputtering the sample for more than an hour, the mass scans in Fig. 2 were taken minutes apart. The ion source output was stable and the observed change in the ion currents of the elements is an effect of laser light and not an effect of sputter time. The measurements were repeated several times on the same sample giving sulfur suppression factors of 10–20. The ion current for Cl^- shown in Fig. 2 was about 10 nA. However, the

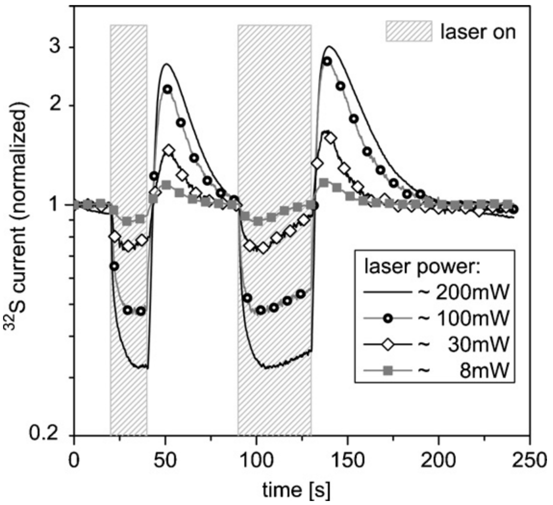

Fig. 3. Time resolved effect on the $^{32}S^-$ current for different laser powers. The plotted currents are normalized individually to the initial currents prior to the first laser shot. The symbols are for identification of various lines and do not represent data points. As little as 8 mW of laser light reduces the sulfur output by 10%. The high sulfur output after removal of the laser light is not a general feature but was present at various times.

transmission of the ion beam apparatus at GUNILLA is only 0.1% [14]. Thus, the estimated total Cl^- current emitted from the source was of the order of 10 μA, i.e. at the same level as at VERA (see below).

When the operational parameters of the ion source were varied, significant changes in the size of the effect could be observed. While the ionizer power given below may not be best suited to quantify ion source conditions, it is the only parameter directly accessible at the two facilities. The Cs currents could not be measured directly nor inferred from cathode currents. Generally, sulfur suppression worked best with low ionizer power of 70–80 W, producing 5–10 μA Cl^- output. Increasing the Cl^- output to 40 μA with 100–120 W of ionizer power reduced the effect on the sulfur to chlorine ratio to approximately 1.5. Even with constant operating parameters of the ion source, i.e. ionizer power, output current, cathode current and cesium oven temperature, the magnitude of the effect differed over time without obvious correlation to the sputter age of the cathode. Therefore, we believe that other source parameters, which could not be measured in the current apparatus, played an essential role. This could be, for instance, the cesium vapor pressure, the sample surface temperature or the cesium coverage on the sample. Thus, the observations are hard to disentangle and they cannot be attributed to a particular parameter.

The dependence of the effect on the laser power was also investigated. The results are summarized in Fig. 3. Already as little as 8 mW laser power at the cathode induced a noticeable change in the sulfur output. The data shows a quadratic behavior of the sulfur reduction as a function of the laser power. We also observe a peculiar effect when the laser light is turned off. While the chlorine current quickly drops to its original value, the sulfur current first increases to a value that is substantially larger than the value before the target was illuminated and then returns to its original value on a time scale of a few minutes. This behavior was observed in about one third of the runs. The reason for this effect is still unclear.

In order to investigate the contribution of photodetachment of sulfur to the effect, the laser source was replaced with a Nd:YAG laser producing radiation with a wavelength of 1064 nm. The corresponding photon energy of 1.17 eV is too small to neutralize any of the ions of interest. Interestingly, both the $^{35}Cl^-$ and the $^{32}S^-$ currents showed the same behavior as with the 445 nm laser, as can be seen in Fig. 4. These results rule out photodetachment of S^- as the cause of the reduction of the sulfur beam. No substantial overshoot was seen when the IR-laser was turned off. The time constant for changes in the source output was close to 20 s.

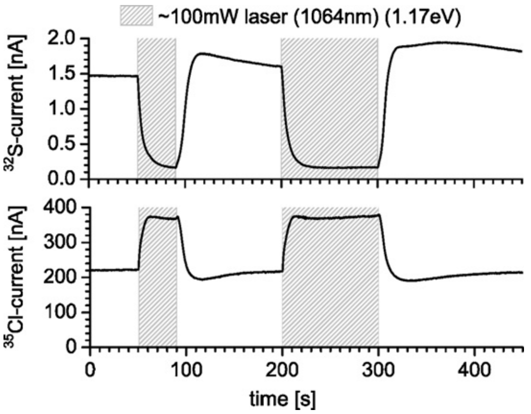

Fig. 4. Response of the $^{32}S^-$ and $^{35}Cl^-$ current to 100 mW IR-laser light. The two scans were obtained one after the other by repeating the experiment at GUNILLA.

3.2. Results with microscopic amounts of sulfur (VERA)

The general trend of the results from GUNILLA could be reproduced at VERA using typical AgCl-samples for AMS, i.e. with sulfur at ppm levels. The sulfur output from the ion source was monitored via the $^{36}S^{7+}$ count rate in a split anode ionization chamber [18]. Since molecules are efficiently destroyed during the stripping process in the tandem accelerator, events in the detector are unambiguously sulfur ions without any molecular background. Reproducing the effect on sulfur also strengthens the argument that molecular background played a very minor role in the results obtained at GUNILLA (see above). Fig. 5 shows a typical response of the source output to the laser light. The source delivered 5–12 μA of $^{35}Cl^-$ current at an ionizer power of 70 W. The response in sulfur had a time constant of several seconds, while the chlorine current took a few minutes to reach equilibrium conditions. The finding that a low ionizer power favors the investigated laser effect was verified.

Even at constant ionizer power the size of the effect varied between different targets. The observed decrease in the sulfur to chlorine ratio ranged from a factor of about 1.3 for all 4 large targets (20 mg AgCl) to a factor of almost 6 for 5 out of 6 small targets (2 mg AgCl). Generally, these changes in sulfur to chlorine ratio were smaller than at GUNILLA, despite a better

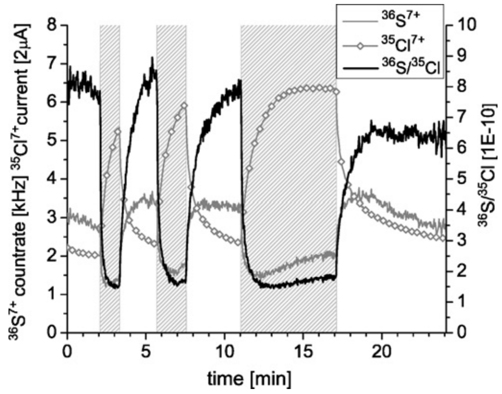

Fig. 5. Typical results with a 2 mg AgCl target at VERA. The chlorine and sulfur output could be monitored simultaneously and changed in opposite ways by applying the laser light. The $^{36}S/^{35}Cl$ ratio stays constantly low even for a 6 min laser shot. Data was recorded every 2 s, the plotted symbols are only for identification of lines.

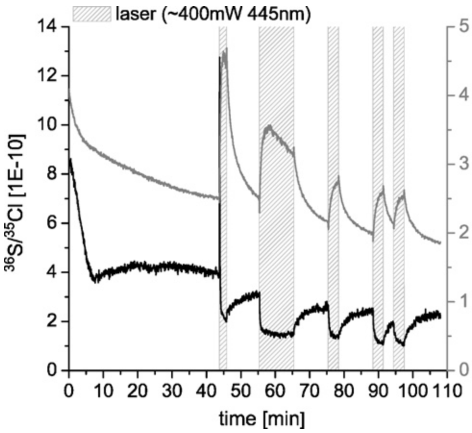

Fig. 6. ^{36}S/^{35}Cl ratio (black, left scale) and ^{35}Cl^{7+} current (grey, right scale) over a 2 h period while turning the laser on and off in periods ranging from a few minutes up to ten minutes (gray areas). Despite prior sputtering for 45 min, the first laser shot has a long-term cleaning effect for sulfur. The response in chlorine output changes with the number of laser shots.

focusing of the laser beam that yielded 400 mW of laser light in a 1 mm × 1 mm area at the target. The explanation could be the less efficient cooling of the cathode via the multi-cathode target wheel compared to the direct cooling of the cathode rod in the single-cathode source used at GUNILLA. It could also be due to different target properties. Apart from initial differences described above, the flat target used at GUNILLA developed a deep sputter crater, whereas no signs of cratering were found on VERA's targets.

A study of 10 identical cathodes was conducted to investigate the reliability of this method for routine AMS measurements. Fig. 6 shows the sulfur to chlorine ratio as well as the chlorine current for a 2 h period of constant sputtering of the same sample, which was illuminated during time periods ranging from 2 to 10 min. Although the lasers used throughout the experiments were cw lasers, the word shot will be used for these minute-long illumination periods in the following. The high sulfur output when first sputtering the sample arises from surface conditions and is present in almost all AgCl-samples. The sulfur to chlorine ratio then stays constant for almost an hour until the laser is applied. Interestingly, the typical sulfur reduction is preceded by a several seconds long "cleaning peak" in sulfur output, but only for the first laser illumination. Afterwards no such behavior is observed. When switching off the laser light, the sulfur to chlorine ratio rises again, although in most cases not to its initial value. Such a long-term cleaning effect was only observed for small AgCl targets with very low sulfur content. Provided that the initial sulfur contamination is sputtered away, the effect of laser light on the isotope currents seems independent of sputter age. Pre-sputtering the sample for an hour did not change the response to laser light. Another effect is that the time constant of the response of the ^{35}Cl^{-} current to the laser light increases with the number of laser shots applied to the cathode from about 20 s in the first shot to about 100 s after 5 shots. The amplitude of the Cl^{-} response also tends to become smaller, typically by 50% after 5 shots. Fig. 7 compares the results of three identical cathodes. It should be noted that another seven cathodes, not shown in figure, showed similar behaviors. For better comparison of the laser-induced effect, the sulfur to chlorine ratios plotted here have been normalized to a curve fitted to the ^{36}S/^{35}Cl values prior to each laser shot. Hence, any permanent decrease of sulfur is not visible in Fig. 7. The same illumination sequence was applied to all three cathodes, except for the first laser shot which was not applied to cathode nr. 2. Comparing the results from this cathode with the others, the magnitude of sulfur to chlorine reduction clearly depends on the number of laser shots already applied or possibly the accumulated illumination time but not on the length of the individual laser shot. The data also shows that the effect is not depending on the sputter age of the cathode before the first illumination. Again, the effect was generally larger at lower source currents.

Finally, the sulfur to chlorine production ratio induced by laser light has been applied in a regular ^{36}Cl AMS measurement at VERA. The sample was a reference material with a nominal ^{36}Cl/^{35}Cl ratio of $(1.57 \pm 0.02) \times 10^{-11}$. (Measured values are expected to be somewhat lower because of roughly 70% detector efficiency for ^{36}Cl.) Initially, the sample was sputtered for ~15 min. Next, two runs of 7 min each with 30 min of continuous sputtering in between, were performed without laser light. Both yielded the same ^{36}Cl/^{35}Cl ratio of $(1.14 \pm 0.02) \times 10^{-11}$, and almost equal ^{36}S/^{35}Cl ratios of $(23.3 \pm 0.05) \times 10^{-11}$ and $(23.9 \pm 0.05) \times 10^{-11}$, respectively. Immediately after the second run the laser was turned on, and after a 2 min wait a run of 7 min was performed with laser light. The ^{36}Cl/^{35}Cl ratio of $(1.11 \pm 0.02) \times 10^{-11}$ agrees very well to the previous runs. The interfering isobar ^{36}S was reduced by a factor of 2.5 to a ^{36}S/^{35}Cl ratio of $(8.99 \pm 0.03) \times 10^{-11}$. This substantial reduction of sulfur is clearly visible in the energy loss spectra from the ionization chamber shown in Fig. 8. Hence, the laser introduces no isotope fractionation (also the ^{35}Cl/^{37}Cl values remained

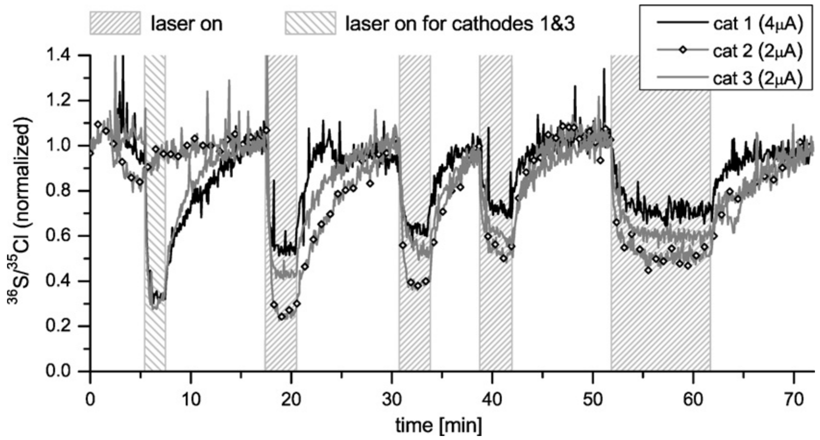

Fig. 7. Comparison of results from three different samples with the same time sequence of laser illumination except for the first laser shot on cat 2. The plotted ^{36}S/^{35}Cl ratios were normalized to a curve fitted to the ^{36}S/^{35}Cl values prior to each laser illumination. The effect of the laser light decreases with the number of laser shots applied and cannot be enhanced by prolonging the illumination time. Sulfur suppression works best at low total source output. Data was recorded every 2 s, the plotted symbols are only for identification of lines. The cathodes were presputtered less than 5 min before data recording started.

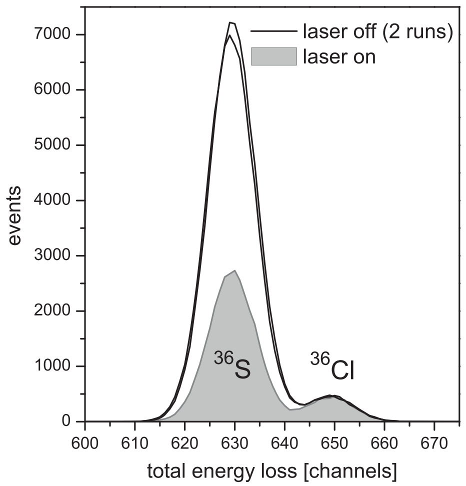

Fig. 8. Total energy loss spectra obtained from the ionization chamber. The laser light reduces the sulfur output from the ion source by a factor of 2.5 but leaves the ^{36}Cl/^{35}Cl unchanged. Results from each run plotted here are normalized to the same accumulated ^{35}Cl^{7+} charge.

constant) but changes only the elemental composition of the negative ion beam.

4. Discussion and outlook

At this point the effect induced by laser light has been studied at two facilities where the influence of several parameters has been investigated. The laser light induced a significant change in oxygen, sulfur and chlorine negative ion production from a AgCl target. However, the physics behind the observed effects remains unclear. The long time constants and the wavelength independence of the effect are strong evidence that no direct photo-induced process on the respective ions is responsible for the observations. In particular, photodetachment of negative sulfur ions can be ruled out since sulfur suppression also worked with an IR-laser. Bulk heating of the cathode by the laser is also unlikely to cause the effect. Even though the laser power is comparable to the radiation power from the ionizer and to the power transfer of the 3 keV Cs beam, an increase of the target temperature by other means, i.e. reduced cooling or higher ionizer power, does not induce similar changes in the sulfur to chlorine ratio. One possible cause could be a localized heating effect in the laser focus on the target surface much stronger than the bulk heating. Alternatively, a microplasma might be formed just in front of the sputter area. However, we have no explanation why this should change the sulfur and chlorine output in opposite ways.

Recently, Vogel et al. [19] suggested that post-ionization of sputtered neutrals by excited neutral cesium plays an important role in cesium sputter ion sources of the Middleton type. While charge transfer cross sections for oxygen (and likely also for sulfur) with excited cesium are one order of magnitude higher than with ground state cesium, the case for chlorine is the opposite. Changing the population of Cs states by laser light may therefore influence the sulfur to chlorine ratio. Nevertheless it remains to be explained, why the two largely different photon energies used yielded similar effects. An explanation could be that neutral cesium (both ground state and excited) is reduced by thermal effects induced by the laser. For chlorine, post-ionization might play a minor role compared to the increased output due to local heating of the sample. Thus, exploring the physics requires probing the target surface temperature and diagnosing the cesium conditions, especially the population of various atomic states. We would like to emphasize that the above discussion is merely an attempt to indicate possible explanations.

However, we believe that the impact on applications is significant. The most important outcome of this work is that the effect induced by laser light can be successfully applied in regular ^{36}Cl AMS measurements (Fig. 8). The experiment clearly demonstrates that this method is a viable technique to reduce the interference of ^{36}S in ^{36}Cl detection without introducing losses in the chlorine beam. While an additional sulfur reduction by a factor of 2.5 may not seem impressive, additional improvements in chemical sample preparation require enormous efforts. Furthermore, implementation of the technique requires no major investments and no major changes to existing AMS facilities.

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