

Fluoride sample matrices and reaction cells — new capabilities for isotope measurements in accelerator mass spectrometry

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Abstract

Two new techniques, which extend the range of elements that can be analyzed by Accelerator Mass Spectrometry (AMS), and which increase its isobar selection capabilities, have been recently introduced. The first consists of embedding the sample material in a fluoride matrix (*e.g.* PbF₂), which facilitates the production, in the ion source, of fluoride molecular anions that include the isotope of interest. In addition to forming anions with large electron binding energies and thereby increasing the range of analysable elements, in many cases by selection of a molecular form with a particular number of fluorine atoms, some isobar discrimination can be obtained. The second technique, for the significant reduction of atomic isobar interferences, is used following mass selection of the rare isotope. It consists of the deceleration, cooling and reaction of the rare mass beam with a gas, selected so that unwanted isobars are greatly attenuated in comparison with the isotope of interest. Proof of principle measurements for the analysis of ³⁶Cl and ⁴¹Ca have provided encouraging results and work is proceeding on the integration of these techniques in a new AMS system planned for installation in late 2012 at the University of Ottawa.

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1. Introduction

A major strength of Accelerator Mass Spectrometry (AMS) in the analysis of low concentrations of isotopes and rare elements is the ability to eliminate molecular isobar interferences [1]. This strength does not extend universally to interferences from atomic isobars, except in the well known cases of ^{14}C - ^{14}N , ^{26}Al - ^{26}Mg and, to a certain extent, ^{129}I - ^{129}Xe . Furthermore, the universality of AMS is limited by the requirement to form negative ions of the analyte sufficiently robust to be accelerated out of the ion source and in the tandem accelerator. This requirement results in a rather short list of rare elements and isotopes usually analysed by AMS: ^3H , ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , ^{41}Ca , Ag, ^{129}I , some platinum group elements and some actinides.

Two new technologies have recently been developed at the IsoTrace Laboratory which provide solutions to the limitations of both anion production and atomic isobar elimination:

- The earlier use of analyte-fluoride compounds in the ion source improved the analysis of ^{41}Ca , with simpler sample preparation, good ion currents and some degree of suppression of the ^{41}K isobar. However, the simple addition of the analyte material to a matrix of PbF_2 in the ion source target has resulted in large anion currents from the ion source, even simpler sample preparation and an intriguing isobar selectivity based on the number of fluorine atoms in the molecular anion selected [2].
- The use of radio-frequency quadrupole ion guides and ion-gas reaction cells in the path of the beam of rare isotopes provides an additional range of highly effective analytical strategies for removing atomic isobars. This has recently been demonstrated for the reduction of $^{36}\text{S}^-$ in beams of $^{36}\text{Cl}^-$ by over six orders of magnitude [3] and for the reduction of $^{41}\text{KF}_3^-$ in beams of $^{41}\text{CaF}_3^-$ by three orders of magnitude [4]. The latter example benefits greatly from the use of both these techniques.

This paper will present an overview of these technologies and discuss some changes in AMS system design that their implementation will require. It will conclude with a description of how these are fitted in to the new Canadian Centre for Accelerator Mass Spectrometry (AMS) at the University of Ottawa.

2. Fluoride matrices for enhanced anion production

In order to provide sufficient flux of the rare isotope or atom of interest, especially at levels approaching 10^{-15} of the abundant species, AMS make almost exclusive use of high power caesium sputter sources [1, 5]. The use of molecular anions from these sources to produce larger beams of elements which do not naturally or readily form atomic anions, taking advantage of the molecular dissociation which occurs during electron stripping in the accelerator high voltage terminal, has been well established [6]. Examples can be found in particular in the group II elements, such as Be and Ca. Usually these take the form of compounds, which can easily be prepared for insertion into the sample position (target) of the sputter source, *e.g.* BeO or CaH₂ [7]. As CaH₂ is difficult to handle in air, Freeman *et al.* suggested the use of CaF₂ [8].

In an exploration of the use of fluoride molecules in the analysis of ¹⁰Be, Zhou *et al.* observed several orders of magnitude of suppression of the ¹⁰B isobar [9]. The later observation by this group of the ability of fluoride compounds in general, such as PbF₂, to form strongly bound molecular fluoride anions [10] motivated a more detailed study of this phenomenon [2]. It was found that in PbF₂, even low levels of impurities could be detected using their fluoride anions. The formation probabilities for anions made from many of the elements in the periodic table were studied by adding small quantities of that element to the PbF₂ target matrix. In the high temperature environment of the sputter source target, fluorine atoms or ions appear to become sufficiently mobile¹ that molecular anions with one more fluorine atom than the normal valence number of the element are preferentially formed. Thus, if the normal formula for the fluoride compound of element X is XF_{*n*}, then the anion XF_{*n*+1}⁻ would be the one most probably produced. As an isobaric interference will usually have a different value for the valence *n*, a simple mass discrimination, as accomplished in most AMS systems by the injection magnet, can significantly reduce this interference. However, as seen in fig. 1 of ref. [2], towards the right side of the periodic table where multiple valences occur more frequently, the uniqueness of this selectivity breaks down. *A fortiori*, in cases such as the lanthanides where the electrons added with increasing atomic number populate inner shells, all these elements show similar characteristics. Nevertheless, in terms of the formation of anions containing these elements,

¹This property of lead fluoride was first reported by Faraday in 1838 [11].

there are few, which cannot be introduced into the accelerator with this technique.

3. Isobar separation using ion-gas reactions

For over a decade, measurements made using inductively coupled plasma mass spectrometry (ICP-MS) have benefited from the use of chemical reaction cells [12] in which ions from the ICP source, usually following a stage of mass selection, are guided through a gas at low pressure, selected so that interferences are removed without attenuating the analyte ion. The adaptation of this technique to AMS is not trivial for the following reasons:

- a) The caesium sputter ion sources used in AMS provide ions beams with much higher current and energy than ICP sources.
- b) The negative ions required for tandem acceleration are usually less robust than the positive ions used in ICP-MS.
- c) The cross sections for destruction and wide-angle scattering of the anions increase rapidly with increasing energy, often limiting the application of this technique to beams of several eV.

Litherland *et al.* [13] outlined a solution to these difficulties with a device known as the Isobar Separator for Anions (ISA) [14]. The beam of rare ions which includes the isotope of interest and any isobars, is decelerated using electric fields, then further reduced in energy by elastic collisions with an inert gas, guided by radio-frequency (RF) quadrupoles (a process known as ion cooling). The beam then passes through the reaction cell, again guided by a RF quadrupole, where the isobars are destroyed by electron transfer or other reactions with the gas in the cell. Beams of the abundant isotopes are measured in off-axis Faraday cups before the deceleration of the rare ion beam. Following the reaction cell, the rare ions are reaccelerated for introduction to the remainder of the AMS system. Based on this design, a prototype was built, but with only one cell in which both cooling and reactions would take place [3]. A schematic drawing of this apparatus is shown in fig. 1.

Initial tests were carried out to explore the applicability of this system for ^{36}Cl analysis, where elimination of the ^{36}S isobar requires tedious sample preparation chemistry and large accelerators (usually $> 6\text{ MV}$). A clue for a suitable reaction gas was provided by the work of Dunkin *et al.* [15], who used a Selected Ion Flow Tube (SIFT) to measure the destruction cross

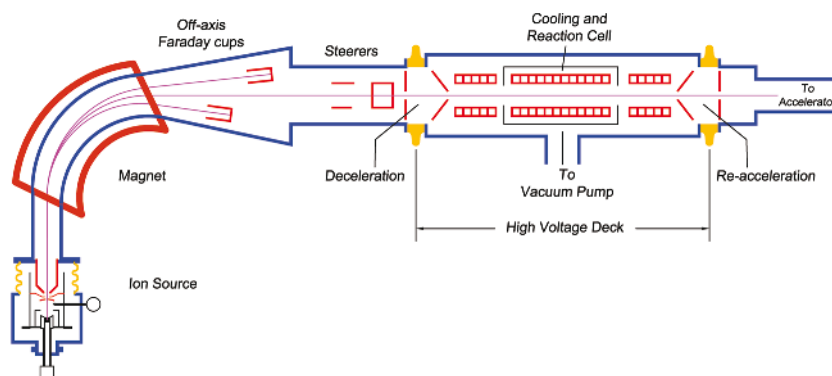


Figure 1: Schematic of the prototype Isobar Separator as used in the measurements described in this presentation. A detailed description of the ion path apertures and RF and DC voltages used is given in ref. [2].

sections for Cl^- and S^- at thermal energies in NO_2 , in connection with atmospheric ozone studies. These cross sections were verified for somewhat higher energies using an electro-spray ion source and a reaction cell as shown in fig. 1 of ref. [13]. Preliminary tests with the ISA prototype [3] used small (nanoampere) beams of the stable isotopes of Cl and S as proxies to establish the attenuation factors as the pressure of NO_2 in the cell was varied. These showed an attenuation of the S^- ions by 7 orders of magnitude at a NO_2 pressure of $8 \mu\text{bar}$. At that pressure, however, there was also an attenuation of the Cl^- of $\sim 70\%$, which has since been attributed to a lack of proper cooling of the Cl^- ions. A plot of attenuation versus NO_2 pressure for these elements is given in fig. 2 of ref. [3]. Tests in which a real mass 36 beam, from a suite of 4 calibration samples², was transmitted through the ISA demonstrated the linearity of the ISA analysis system over a range in $^{36}\text{Cl}/\text{Cl}$ ratios from 4×10^{-11} to 4×10^{-13} [4]. They also showed the ability of this system to remove molecular in addition to the atomic isobar interferences with the destruction of the ^{12}C trimer anion.

Another isobar pair investigated using the prototype ISA was ^{41}Ca and ^{41}K ; ^{41}Ca is used as a tracer in biomedical research. In this case, the fluoride molecular anions were used [4]. For Ca, the predominant anion is CaF_3^- whereas for K it is KF_2^- (see fig. 1 of ref. [2]), so CaF_3^- was selected in the injection magnet and this molecular anion was sent through the ISA. Again, for the attenuation tests, small beams of the stable isotopes were used as proxies. Although a small amount of KF_3^- is produced in the sputter source

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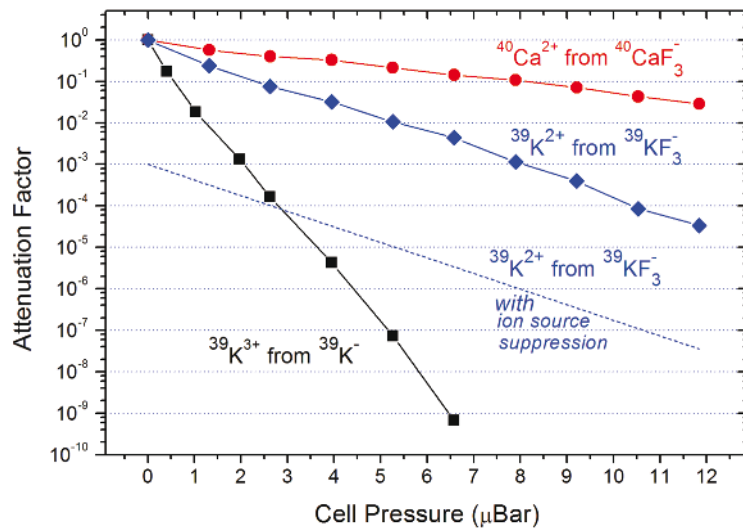


Figure 2: Plots of the attenuation of the ion flux measured in the AMS final detector or in a Faraday cup immediately before it as a function of NO_2 pressure in the reaction cell. The “from” species are the anions from which the detected ions were produced. The dashed line is a linear fit to the $^{39}\text{K}^{2+}$ data multiplied by the ion source suppression factor for $^{39}\text{KF}_3^-$ relative to the production of $^{40}\text{CaF}_3^-$ (0.001). As noted in the text, stable isotopes were used as proxies for the rare radioactive species for more efficient testing of the reaction cell.

($\sim 1\%$ of the yield of CaF_3^- from the source), it was expected that the KF_3^- would be a less robust anion and would be destroyed in the ISA reaction cell. The attenuation of the KF_3^- , shown in fig. 2 was not as impressive as that of the S^- but was still greater than 4 orders of magnitude at $11.5 \mu\text{bar}$ of NO_2 . When compared with the attenuation of the CaF_3^- , the relative attenuation factor was ~ 1000 . However, when coupled with the attenuation of the KF_3^- in the ion source a total relative attenuation factor of $\sim 10^6$ is obtained, as shown by the dashed line in fig. 2.

4. Discussion

Although these measurements have produced encouraging results, a great deal of development work is needed to transform them into analytical techniques. The decision to equip the prototype with only one cell for both cooling and reactions has been shown to work in some cases, but is expected to be the cause of a significant fraction of the loss of Cl^- ions, as its destruction cross section is a sensitive function of energy (fig. 2, ref. [13]). A

two-cell system has been built and will be tested in the near future. In addition, tests of other reaction gases, which might cause less attenuation of the analyte ion or more effective attenuation (*i.e.* at a lower pressure) of the interfering anion, are needed. Similar searches for an inert cooling gas will be needed, but initial tests indicate that a light, inert gas will be best suited for this purpose [4].

Further tests on specific elements of interest are also needed for the method in which ion source targets are made from fluoride matrices, in particular to determine the most appropriate compound by which to introduce the analyte element into the matrix. While this is not so critical for lighter elements, for the heavier elements, the possibility of introducing molecules, which result in interferences or near interferences in the post accelerator system, is increased.

The use of molecular anions containing multiple fluoride atoms increases the mass of the ion, which must be analysed before injection into the accelerator. This means that not only must the bending power of the injector magnet be greater, but also that the resolution of this magnet has to be greater to eliminate too large a contribution from the beam of a much more abundant neighbouring isotope. For example, in the AMS system currently being built for the University of Ottawa, the injection magnet has a mass-energy product of 12 MeV-AMU, sufficient to inject $^{244}\text{PuF}_5^-$ at an energy of 35 keV. This is accomplished with a resolution > 800 at a mass of 265 AMU. A more detailed description of this system is given in ref. [16].

5. Conclusions

The use of fluoride matrices to enhance the production of anions in a sputter source is a technique, which shows significant promise for augmenting the range of elements that can be analysed by AMS. Much detailed work will be needed to identify the optimum use of carrier compounds and AMS parameters in the case of each specific element to be studied. The same is true for the reaction cell procedure exemplified by the ISA. However, in this case, the areas of research include the selection of cooling and reaction gases as well as the usual AMS strategies.

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