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On-line ion chemistry for the AMS analysis of ^{90}Sr and ^{135,137}Cs

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The analysis of ^{90}Sr by AMS has so far required the use of very large tandem accelerators in order to separate the isobar ^{90}Zr by the rate-of-energy-loss method. The analysis of ^{135,137}Cs by AMS has never been attempted as the separation of the isobars ^{135,137}Ba by the traditional method requires even higher energies, so that this approach would become prohibitively expensive for routine analysis. Following the successful demonstration of Cl^-–S^- separation by the Isobar Separator, the same apparatus was used to test the separation of other pairs of isobars. Surprisingly effective results were obtained with NO_2 gas in the cases of SrF_3^-–ZrF_3^- and CsF_2^-–BaF_2^- separations. Reduction factors of $\sim 4 \times 10^{-6}$ for ZrF_3^-/SrF_3^- and $\sim 2 \times 10^{-5}$ for BaF_2^-/CsF_2^- were measured. SrF_3^- and CsF_2^- are both super-halogen anions and are preferentially produced in the ion source rather than ZrF_3^- and BaF_2^- when using the PbF_2 matrix-assisted method. Reduction factors for ion source production with such targets of $\sim 3 \times 10^{-5}$ for ZrF_3^-–SrF_3^- and $\sim 5 \times 10^{-4}$ for BaF_2^-–CsF_2^- were found. The combined methods would suggest a theoretical detection sensitivity for ^{90}Sr/Sr $\sim 6 \times 10^{-16}$, ^{135}Cs/Cs $\sim 7 \times 10^{-15}$ and ^{137}Cs/Cs $\sim 1 \times 10^{-14}$, assuming 10 ppm Zr and Ba contamination in the AMS targets. In addition to the earlier Cl^-–S^- separation work, these measurements further illustrate the potential of on-line ion chemical methods for broadening the analytical scope of small AMS systems.

1. Introduction

The recent discharge of nuclear fuel material into the environment from the Fukushima Daiichi power reactors [1] has once more emphasized the need for rapid and sensitive analysis of fission products in environmental samples. In terms of both their large fission yield and their significant danger to biological systems, the radioisotopes of strontium and caesium both present very serious hazards. Strontium-90, with its half life of 28.87 years and low β decay energy of 54 keV mimics calcium in biological systems and thus becomes concentrated in bone. Caesium-137 has a similar half life, 30.08 years and slightly more energetic β decay energy of 187 keV, followed by a 661 keV γ from the decay of the daughter state in ^{137}Ba. Caesium-135 has a half life of 2.3×10^6 years and decays with a 76 keV β. Caesium isotopes mimic sodium in biological systems.

In the case of ^{137}Cs, the γ-ray from the daughter product makes its detection relatively simple. However for ^{90}Sr and ^{135}Cs, their low energy β decays make their detection by radiometric methods very difficult and quite insensitive. For ^{90}Sr samples, the detection of the weak β decay is masked by the more energetic β from ^{89}Sr until the latter has decayed away (half life 50.5 d). For ^{135}Cs samples, a similar masking occurs from the more energetic β from ^{137}Cs. The use of ICP-MS to count these isotopes directly has both simplified the work required for sample preparation and analysis and has improved the detection limits. For ^{90}Sr, Taylor et al. [2], using O_2 gas in a reaction cell to suppress the ^{90}Zr interference, achieved detection limits of 40 fg/g[1] in plant material and 3 fg/g in water. For ^{135}Cs, this group achieved 200 fg/g for solid samples [3]. Liezers et al. [4] achieved 2 fg/ml for liquid samples by using in-line chromatography to remove the Ba interference. However, in all these cases, molecular interferences limited the detection of lower levels.

Despite its ability to deal with molecular interferences, the measurement of ^{90}Sr provided major challenges for AMS. Korschinek et al. [5] used an MP tandem with terminal voltage V_T = 14 MV, a gas-filled Q3D magnetic spectrograph and a time-of-flight system to reach a detection limit of 2.6 pg/g. Three years later, Paul et al. [6] using SrH_2 targets, a 12UD Pelletron with V_T = 12 MV, time-of-flight and a four element gas ionization detector (3 anodes + a Si residual energy detector) reported a limit of 7.5 fg in a laboratory blank samples. Recently, Tumey et al. [7,8] using SrF_2 targets, an FN tandem at V_T = 9.25 MV, foil stripping to charge state 11^+ and a gas ionization detector with a silicon nitride

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[1] Unless otherwise indicated, detection limits are quoted as mass of atoms measured per mass of original sample used.

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window and three anodes designed to optimize the measured energy loss difference between ^{90}Sr and ^{90}Zr.

This resulted in a detection sensitivity of 0.6 fg in the 1 mg of Sr blank target material used. It should be noted that there is a difference in the usage of the term "detection limit" between the ICP-MS work [2–4] (measured with respect to the quantity of material used for a process blank, which includes all preparation chemistry) and the AMS [5–8] work (usually measured on a target made directly from background material. This renders comparison of these techniques difficult. We are unaware of any attempts to analyze Cs isotopes by AMS.

Recent work at IsoTrace on the use of fluoride ion source target matrices for enhanced anion production and isobar suppression [9] and on the use of radio-frequency (RF) ion guided reaction cells (the Isobar Separator for Anions, or ISA) [10,11] in the low energy analysis line of the AMS system have demonstrated that when used together, these techniques can provide a significant increase in isobar suppression. In this paper we present measurements on Sr with its isobars Zr and Y, and Cs with its isobars La and Ba.

2. Experimental results

As in the earlier work [9] targets were made by mixing the compound of interest with PbF_2 in a ratio of 1:5 by volume. The compounds used for these measurements were SrF_2, YF_3, ZrF_4, BaF_2 and LaF_3. We initially attempted to use targets made with CsN_3 and PbF_2 to produce CsF_2^- but these targets disintegrated when sputtering began. This is not surprising considering that CsN_3 decomposes at 301 °C, releasing large quantities of N_2 gas. However, sufficient beams of CsF_2^- were obtained by using the accumulated Cs from the primary beam and any PbF_2 matrix. Compound and matrix materials were well mixed in a round-bottomed glass tube and pressed into a 2.4 mm diameter hole in a stainless steel holder.

Measurements of the relative anion production from these targets were carried out using the 834 SIMS type source on the IsoTrace system with 17.5 keV Cs+ primary beam energy and 10 kV acceleration voltage applied to the anion beam. Relative intensities for the atomic and molecular anions produced from the Sr–Y–Zr and Cs–Ba–La groups are listed in Table 1. As the targets were made with similar proportions of the elements of interest and PbF_2, and as the total fluoride molecular anion currents from each element in the group were similar, this data indicates that the ZrF_3^- production is suppressed by a factor 3×10^{-5} with respect to that of SrF_3^-. Similarly, BaF_2^- is suppressed by 5×10^{-4} with respect to CsF_2^-.

Measurements of the isobar suppression using the ISA were carried out on the ISA injection line which includes a single target high current ion source (860 type) and a wide gap 90° analyzing magnet. A similar approach as that described for the suppression of the S^- isobar for the analysis of ^{36}Cl in Ref. [10] was used. As the interactions within the reaction cell are chemical, low current ($\sim$10 nA) beams of the abundant isotopes rather than particles of the rare isotope were used to demonstrate the suppression of the undesired element. The details of the ISA are provided in Refs. [10] and [11], so only changes to the system parameters are reported here. The DC voltages in the ISA column remained the same; however, the RF voltages on the ion guides had to be increased: for the decelerating quadrupole, $V_{RF(p-p)} = 780$ V and for the cell quadrupole $V_{RF(p-p)} = 880$ V, to compensate for the greater mass of the ions. At these voltages, the Mathieu stability parameter q, an indication of the depth of the potential well formed by the RF quadrupole [12] is $\sim$0.1.

Table 1
Relative anion production yields for the atomic and fluoride molecular anions listed in the left column. The values for each element are given as a percentage of the total yield of fluoride molecular anions for that element. Measurement for the anion species in this table were made using the IsoTrace SIMS-type General Ionex 834 ion source with a constant caesium primary beam current of 10 μA. Currents of the most abundant fluoride anion were typically 100 nA.

M	Sr	Y	Zr	Cs	Ba	La
M^-	0	0.0002	0.0005	0.001	0	0.00004
MF^-	0.05	0.007	1.6	0.3	0.09	0.04
MF_2^-	0.1	0.03	0.02	99.7	0.05	0.3
MF_3^-	99.9	0.002	0.003		99.9	0.4
MF_4^-		100	0.002			99.3
MF_5^-			98.3			

For the Sr–Y–Zr measurements, 10 nA beams of $^{88}SrF_3^-$, $^{89}YF_3^-$ and $^{90}ZrF_3^-$ were magnetically selected, collimated, decelerated to $\sim$10 eV and transmitted to the reaction cell containing NO_2 gas. The molecular anions transmitted by the ISA were then introduced to the accelerator, stripped in argon, and the +2 atomic ions of the metals were detected in the Faraday cup following the high energy magnetic analyzer. Fig. 1 shows a plot of the attenuation of these ions as a function of the pressure of NO_2 in the cell. At a pressure of 0.5 Pa NO_2, the relative attenuation of ZrF_3^- with respect to SrF_3^- is 4×10^{-6}. In the calculation of the relative attenuation factors, similar stripping yields and transmission were assumed for the element of interest and the isobar surrogates; these are not expected to vary significantly in this mass range. It should be noted that the steep slope of the ZrF_3^- suppression in the 0–0.2 Pa pressure range indicates a large destruction cross section for this molecular anion in NO_2. The YF_3^- requires a somewhat higher pressure of NO_2 to reach equilibrium (Fig. 1), indicating a lower destruction cross section; at a pressure of 0.7 Pa, the YF_3^- attenuation factor is 5×10^{-5}.

For the Cs–Ba–La measurements, 10 nA beams of $^{133}CsF_2^-$ and $^{135}BaF_2^-$ were similarly transmitted to the reaction cell. Insufficient beams of LaF_2^- could be obtained to make measurements in a finite period of time. Again NO_2 gas was used as the reaction gas and following the accelerator the charge +4 atomic ions were selected for analysis. The attenuation plot for Cs and Ba are shown in Fig. 2. At a cell pressure of 0.6 Pa NO_2, the attenuation of BaF_2^- with respect to CsF_2^- is 2×10^{-5}.

3. Discussion

The attenuation factors measured above for both the fluoride matrix anion production and the NO_2 reaction cell in the ISA are

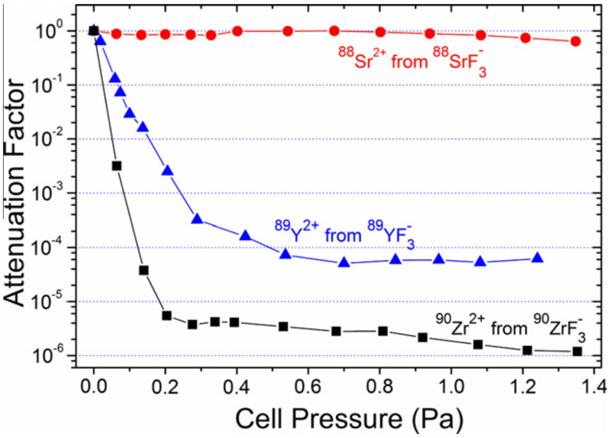

Fig. 1. Transmission of the triple fluoride anions of Sr, Y and Zr as a function of pressure of NO_2 in the ISA reaction cell, normalized to the transmission at 0 Pa cell pressure. The charge state +2 atomic ions were measured in a Faraday cup following the analyzing magnet after the accelerator. Uncertainties in the attenuation factor are smaller than the data points.

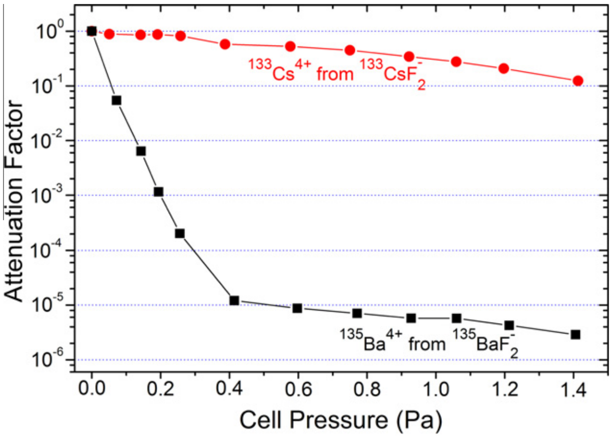

Fig. 2. Transmission of the double fluoride anions of Cs and Ba as a function of pressure of NO_2 in the ISA reaction cell, normalized to the transmission at 0 Pa cell pressure. The charge state +4 atomic ions were measured in a Faraday cup following the analyzing magnet after the accelerator. Uncertainties in the attenuation factors are smaller than the data points.

individually quite useful. Indeed, the work by Tumey et al. [7,8] appears to have benefitted from the use of SrF_3^- to reduce the Zr interference. If these techniques are used in combination, significantly more powerful interference reduction is possible.

For the Sr–Y–Zr system, ^{90}Zr is the likely to be the only external source of isobaric contamination as ^{90}Y has a half life of 64 h. As ^{90}Y is the daughter product of ^{90}Sr, it is likely to be present at levels only as high as 2.54×10^{-4} of the ^{90}Sr concentration assuming that the sample has been intact for the >300 h needed to reach secular equilibrium. If this is the only source of ^{90}Y, its presence could be neglected in ^{90}Sr analysis, but is included in this discussion for completeness. Table 2 summarizes the attenuation factors for both fluoride matrix and ISA techniques and shows the expected relative suppression of the contribution to mass 90 flux from both the above level of Y and a Zr contamination level of 10 ppm.

A similar summary and estimates for the analysis of ^{135}Cs and ^{137}Cs are also given in Table 2. Although the AMS analysis of Cs may appear complicated due to the ubiquitous use of Cs for sputtering it is relatively simple to incorporate into the target material a yield tracer such as ^{134}Cs and use the analysis techniques developed for the Pu isotopes by Zhao et al. [13]. Alternatively, Rb could be used instead of Cs to form the primary beam, although it may be difficult to obtain Rb which contains a low enough level of Cs. It should be noted, because of the possible effect of variations in target composition and homogeneity of component mixing, on the ratio of the production of the molecular anions (column 4 in Table 2), that these suppression values should be considered approximate. However, they provide a useful indicator for the design of measurement protocols involving these techniques.

In both Figs. 1 and 2, the same characteristic plateau in the suppression curve of the unwanted isobars occurs ("hockey stick shape") as in the S^- curve in chlorine analysis [10]. The reason for the existence of this plateau and for the variation in its level for each elemental or molecular species is a subject for future investigation.

Table 2
Attenuation levels for the techniques discussed in this paper and the calculated expected background flux relative to the isotope of interest for a contamination level of the isobar element in the target of 10 ppm (1×10^{-5}). The ^{90}Y level present is based on the amount generated from ^{90}Sr at secular equilibrium (see text). As the matrix and Isobar Separator attenuation factors are based on ion source current measurements, the uncertainties in these numbers are of the order of ±10%.

Isobaric contaminant	Elemental level present	Isotopic abundance of isobar	Attenuation: fluoride matrix	Attenuation: Isobar Separator	Overall flux relative to analyte isotope
For ^{90}Sr analysis					
^{90}Y	2.54×10^{-4}	Not applicable	2×10^{-5}	5×10^{-5}	2.4×10^{-13}
^{90}Zr	1×10^{-5}	51.5%	3×10^{-5}	4×10^{-6}	6×10^{-16}
For ^{135}Cs analysis					
^{135}Ba	1×10^{-5}	6.6%	5×10^{-4}	2×10^{-5}	7×10^{-15}
For ^{137}Cs analysis					
^{137}Ba	1×10^{-5}	11.2%	5×10^{-4}	2×10^{-5}	1×10^{-14}

The earlier successful demonstration of Cl^-–S^- separation using the ISA opened up the possibility of ^{36}Cl analysis at low terminal voltages. These measurements further illustrate the potential of on-line ion chemical methods for broadening the analytical scope of small AMS systems. The engineering implementation of this technology into AMS systems is now ready to be pursued.

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