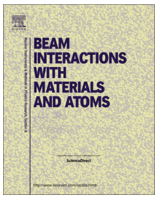
Nuclear Instruments and Methods in Physics Research B xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Isobar Separator for Anions: Current status

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ARTICLE INFO

Article history:
Received 16 December 2014
Accepted 20 March 2015
Available online xxxx

Keywords:
Isobar Separator for Anions
Isobars
Accelerator Mass Spectrometry
ISA

ABSTRACT

The Isobar Separator for Anions (ISA) is an emerging separation technique of isobars applied first to the selective removal of ^{36}S from ^{36}Cl, achieving a relative suppression ratio of 6 orders of magnitude. Using a radio-frequency quadrupole (RFQ) column incorporating low energy gas cells, this innovative technique enables the use of a wide range of low energy ion–molecule reactions and collisional-induced dissociation processes for suppressing specific atomic of molecular anions with a high degree of selectivity. Other elemental pairs (analyte/isobar) successfully separated at AMS level include Ca/K, Sr/(Y, Zr), Cs/Ba, Hf/W and Pu/U. In view of these initial successes, an effort to develop a version of the ISA that can be used as a robust technique for routine AMS analysis has been undertaken. We will discuss the detailed layout of a practical ISA and the functional requirements that a combined ISA/AMS should meet. These concepts are currently being integrated in a pre-commercial ISA system that will be installed soon at the newly established A.E. Lalonde Laboratory in Ottawa, Canada.

1. Introduction

The very origin of the Isobar Separator for Anions for AMS can be traced back to a report by Dunkin, Fehsenfeld and Ferguson [1] in the early 1970s, who reported the rate constants for the electron transfer reaction of the anions Cl^- and S^- with NO_2 in near thermal conditions (<1 eV).

$$Cl^- + NO_2 \rightarrow Cl + NO_2^- \quad \text{rate constant} :< 6 \times 10^{-12}\ cm^3/s \qquad (1)$$

$$S^- + NO_2 \rightarrow S + NO_2^- \quad \text{rate constant} : 1.3 \times 10^{-9}\ cm^3/s \qquad (2)$$

These rate constants translate to an endothermicity of 1.34 eV for reaction (1) and exothermicity of 0.2 eV for reaction (2). The difference between these rate constants is sufficient to expect the preferential and near complete destruction of the ion S^- via charge transfer to NO_2, in appropriate energy conditions. The potential of this pair of reaction to selectively suppress the stable isotope ^{36}S in the determination of ^{36}Cl by AMS had been known previously, but the main difficulty has been to selectively enable reaction (2) on an AMS injection line where energy of anions in the analytical beam are typically found in the range from 20 keV to 60 keV. At these energy levels, far from thermal, London interactions between ions and neutral molecules become negligible and the rate constant of reaction (2) collapse. A practical solution to this problem was reported first in 2007 by the Isotrace Group in Toronto in collaboration with IONICS Mass Spectrometry (Bolton, Ontario, Canada) [2], using hardware that included a single pressurized radio-frequency quadrupole (RFQ) gas cell derived from low energy triple-quadrupole mass spectrometers built by IONICS. This rather primitive proof-of-concept system, integrated between the separation magnet and the tandem accelerator in an AMS injection line, almost immediately demonstrated a very effective 6 order of magnitude suppression of sulfur relatively to chlorine. A workable transmission efficiency of about 18% for the unreacted chlorine was obtained. The suppression of ^{41}K from ^{41}Ca on the same platform was reported in subsequent papers [3,4], initially with a relative suppression ratio of 10^3, but reaching 10^4 after the addition of a gap on the RFQ. Contrary to ^{36}Cl and ^{36}S, which are ionized as atomic anions by the sputter source, ^{41}Ca and ^{41}K are ionized as their fluorides anions: CaF_3^- (a superhalogen anion of general formula MX_{n+1}^- where X is a halogen and n is the normal valence number of metal M) and KF_3^-, respectively, using the in-source fluorination method assisted by PbF_2 originally developed at the Isotrace Laboratory [4]. KF_3^-, although belonging to a new class of superhalogen of formula MX_{n+2}^- recently identified

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http://dx.doi.org/10.1016/j.nimb.2015.03.059
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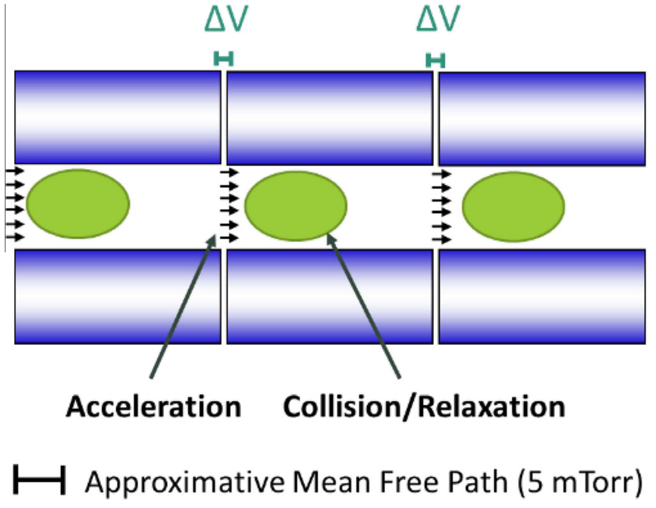

Fig. 1. Schematic view of the acceleration and collision/relaxation zones in a segmented RFQ cell filled with a low mass collision gas at a pressure of approximately 5 mTorr (6.7×10^{-6} mbar) and temperature of 298 K (not to scale).

[5], is nevertheless more fragile than CaF_3^-. KF_3^- is preferentially destroyed in the ISA using a variety of gases, some unreactive such as argon, indicating that the suppression likely proceeds via selective molecular fragmentation. The ISA has also proven to be capable of impressive selective isobar suppression in the determination of the other long-lived radionuclides ^{90}Sr, ^{135,137}Cs [6] and ^{182}Hf [7]. These ions and their isobars are also ionized as fluoride anions, similarly to the Ca/K pair, with a relative degree of isobar suppression exceeding 10^6 for some isobars.

In this paper we will introduce a new concept for a commercial version of the ISA designed to handle equally well the separation of the Cl/S and Ca/K pairs. The two separation processes are in many ways opposing cases each highlighting specific strengths and weaknesses of the proof-of-concept system used so far. It is assumed, with our current knowledge, that such an ISA has reasonable chances to handle well the separation of more isobars, through separation methods already known or still to be discovered. Moreover, a modular design will allow the development and easy implementation of specialized columns designed to optimize the suppression of specific isobars.

2. Principle of operation

In standard AMS injection lines, anions are produced and transported in the form of a beam typically accelerated to energies up to 60 keV. In contrast, anions transiting through the RFQ column of the ISA are confined in an oscillatory electric field and are transported in bulk at low energy (<10 eV). The capability of the ISA to transport anions at near thermal energy through rarefied gases is the key characteristic enabling a highly efficient suppression of isobars. To achieve compatibility with standard AMS systems, deceleration and acceleration stages located at both end of the RFQ column of the ISA accomplish the conversion from beam transport regime to bulk transport, then back again to beam transport. In practice, the analytical beam generated from the sputter source and emerging from the first separation magnet is decelerated to an energy level (<100 eV) allowing anions to be fully trapped in the RF energy well in the first stages of the RFQ column. Once bulk transport regime through the RF field is achieved, a great level of control can be exerted on the captured anions through the application of electrostatic fields in the RFQ column, either applied through discrete electrodes or apertures, or as bias voltages on the RFQ ion guides. In the ISA, we use this control to move anions forward through the column and have them interact with rarefied gases at near thermal energy. By properly selecting gases and precisely controlling the energy of ion–molecule interactions, the analyst can very effectively suppress a variety of isobars with a high degree of selectivity. A new DC beam, analytically clean and of same energy as the original one, is reformed from the unreacted anions emerging from the exit of the RFQ column, reestablishing beam transport regime up to the entry of the tandem accelerator. The beam in the injection line is therefore split in two independent sections by the ISA; as all phase space information of the original beam is normally destroyed by the trapping of ions in the RF energy well, as well as by multiple ion–molecule collisions occurring through the pressurized sections of the RFQ column.

Because of limitations of DC simulation tools when RF fields are involved and the complexity associated with ion transport in gases [8], it is problematic to accurately model the trajectory of anions as they transit through the different transport regimes and pressure regions of the ISA. While a simulation tool like SIMION can accurately predict the free trajectory of individual ions traveling through electrostatic fields, its predictions are often invalidated by space charge effects when ions collectively confined in an oscillatory field are considered. Moreover, in the pressurized regions of the ISA ($P > 10^{-6}$ mbar), ion trajectory calculation must be combined with a Navier–Stokes fluid dynamic model to correctly describe the local (or micro) motion of ions in oscillatory fields [9]. This combined modeling generally predicts a suppression of ion oscillations by gas dampening, a prediction that actually has favorable implications for the ISA. Gas dampening of ion oscillations is at the origin of phenomena routinely observed and exploited in modern triple-quadrupole mass spectrometers, notably the improved focusing – achieved by loss of axial kinetic energy – of ion trajectories along the main axis of pressurized RFQ ion guides, also called collisional focusing [10], and a reduction of the influence of reflecting fringe fields typically found near the entrance and exit of pressurized RFQ cells [11]. Armed with this knowledge, the design of the RFQ column of the ISA can be optimized by staging correctly the different pressure zones and gas types along the main axis of the column. The goal is to enhance the capabilities of the ISA to capture and transmit analytical anions and to suppress isobars.

3. Description of the pre-commercial ISA

The proposed design for the pre-commercial ISA incorporates the most recent advances in the manufacturing processes of triple–quadrupole mass spectrometers and draws from the decades-long experience that some of the authors (G.J. and L.C.) have in designing pressurized RFQ systems. The design of the lensing system in the deceleration and acceleration stages were also greatly improved by the Lalonde Laboratory team. This new design use a segmented RFQ, an approach originally developed to improve the handling and transmission of fragile organic molecules in low energy mass spectrometers [12,13]. In that approach, short gaps of 1–2 mm are created at regular intervals along the RFQ column over the length of the gas cell, effectively creating short RFQ sections isolated for each other. These RFQ segments are capacitively coupled together to form an uninterrupted RF field along the main axis of the segmented column. Each segment can be biased to a discrete voltage that can be collectively chosen to produce an electrostatic field between segments, effectively creating a stepwise gradient field along the main axis. The axial field provides several advantages that are of value to the operation of the ISA. In a segmented RFQ column, the axial field generated between segments allows the ions to maintain a minimum velocity through the

Please cite this article in press as: J.-F. Alary et al., Isobar Separator for Anions: Current status, Nucl. Instr. Meth. B (2015), http://dx.doi.org/10.1016/j.nimb.2015.03.059