

MULTIPLE ION COUNTING IN NOBLE GAS MASS SPECTROMETRY. U. Ott^{1,2}, B. Baecker^{2,3} and M. Trieloff⁴, ¹University of West Hungary, Károlyi Gáspár tér 4, 9700 Szombathely, Hungary (e-mail address: uli.ott@mpic.de); ²Max-Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany; ³UCLA, 595 Charles Young Drive East, Los Angeles, CA 90095-1567, USA; ⁴University of Heidelberg, Im Neuenheimer Feld 234-236, D-69120 Heidelberg, Germany.

Introduction: Noble gases are the trace elements *par excellence*, and unlike for more abundant elements in extraterrestrial materials sensitivity is - at least for Kr and Xe - more of a concern than ultimate precision, which is often limited just by the number of atoms in a sample. This is especially so in small samples like micrometeorites, interplanetary dust particles and presolar grains, where so far only few successful analyses of Kr and Xe have been performed.

There are various possible solutions to this problem. One is use of a compressor ion source [1], which enhances the pressure in the ionizing region and which has been successfully employed in, e.g., the study of Ne in presolar SiC and graphite grains [2, 3]. Another is resonance ionization coupled with a time-of-flight rather than a magnetic mass spectrometer (RIMS) [4, 5]. Both methods produce optimum yields, but currently are useful only for a subset of the noble gases: the light ones in case of the compressor ion source, because Kr and Xe are too rapidly depleted during measurement; and extremely small Kr and Xe amounts in case of RIMS because of the lack of suitable lasers for the lighter gases and the size of the ion signals that can be handled in TOF mass spectrometry.

Multiple Ion Counting (MIC): A “compromise” approach is conventional noble gas mass spectrometry coupled with a multiple ion counting detection system. While not specialized, thus not providing the ultimate sensitivity in each individual case, it still is an across-the-board improvement compared to traditional noble gas mass spectrometry. In particular, due to shorter measuring time, the required extrapolation of amounts and ratios to the time of gas inlet is less critical.

Our *Noblesse* (Nu Instruments) noble gas instrument now hosted in Heidelberg is equipped with a multiple ion counting detector (Fig. 1; eight channeltrons, plus a Faraday cup for larger signals [6]) similar to the one employed by [7]. For Xe, the detector allows simultaneous measurement of the even-numbered or the odd-numbered isotopes, so a two step measurement routine is required. The same is true for Kr, if all isotopes are to be measured, while omitting ⁷⁸Kr allows all others (like in Ne and Ar) to be measured simultaneously in one step.

In our analyses so far, full multiple ion counting has been used for Kr and Xe. In case of Ar, isotopes ³⁶Ar and ³⁸Ar were mostly measured on the same channel-

tron, with ⁴⁰Ar generally measured using the Faraday cup. For Ne MIC was used for the interference masses (mass 18 was measured simultaneously with ²⁰Ne, and also masses 40 and 44 were measured simultaneously).

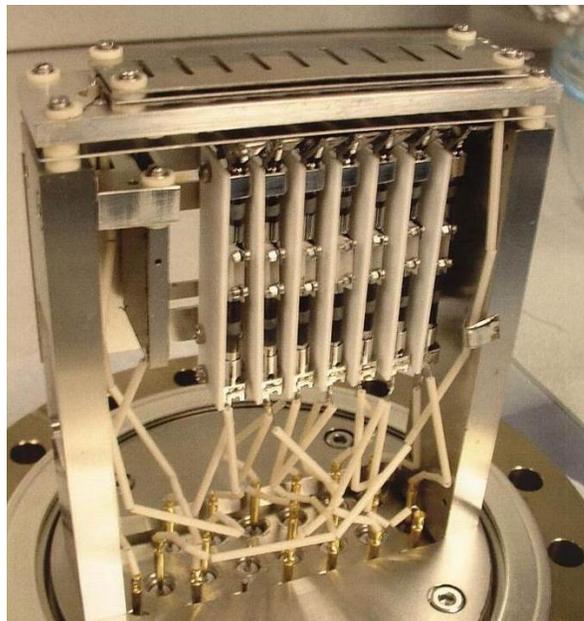


Fig. 1. Multi detection system in *Noblesse* comprising 8 channeltrons and a Faraday cup.

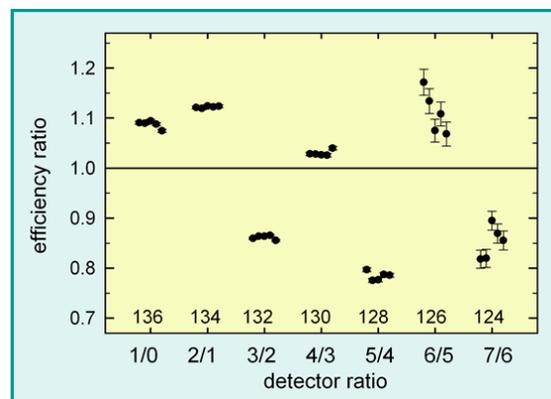


Fig. 2. Ratio of efficiencies for neighboring channeltron detectors determined during five air calibrations over a period of about a month. Indicated is also the respective ion beam used to determine the ratio.

Cross calibration. A basic problem inherent to MIC is the need for cross-calibration of the different detectors. Fig. 2 shows the relative detection efficiencies of neighboring channeltrons as determined over a

period of about a month, using our air Xe standard and switching the indicated masses between the channeltrons. As apparent, relative efficiencies may differ up to 50%. While the factors stay relatively constant most of the time, we have also experienced periods of drift and therefore have considered an alternative measurement protocol, that of “internal calibration”.

For this we add to the standard routine a third measurement step (step #2), where like in step #1 the even isotopes are measured, but in a different setup. Step #3, as in the standard routine, measures odd-numbered ^{129}Xe and ^{131}Xe (Table 1). The ratio of the signals for a given isotope measured on the different channeltrons during the actual analysis is then used as a factor in calculating the isotopic ratios.

channeltron #	step 1	step 2	step 3
0	136		
1	134	136	
2	132	134	131
3	130	132	129
4	128	130	
5	126	128	
6	124	126	
7		124	

Table 1: Three-step measurement routine used for “internal calibration”.

A problem with this is that only efficiency ratios between neighboring channeltrons are directly determined and for ratios of isotopes further apart the product of several correction factors must be used, which inflates analytical errors. For isotopes 129 and 131 no efficiency correction is required since in step 3 they are measured on the same detectors as the normalizing isotope ^{132}Xe (detector 2 in step 1 for $^{131}\text{Xe}/^{132}\text{Xe}$; detector 3 in step 2 for $^{129}\text{Xe}/^{132}\text{Xe}$). Overall precision with and without internal correction is similar as long as the system is stable. Advantages of the three-step routine, however, are a) that raw ratios are already close to the true ones (Fig. 3); and b) that it is rather straightforward to recognize unusual behavior that may lead to flawed results.

Cross talk. A comparably minor effect is cross talk between the different detectors. For our current setup this was found to be typically on the order of half a percent on the neighboring channeltrons, being slightly asymmetric (somewhat higher on the high-mass side). Cross talk effects on the detectors farther away are much smaller. Since, for samples isotopically similar to the standard, the correction is automatically included in the “effective” discrimination factors, we correct sample data according to the difference only. Usually this correction is much smaller than analytical uncertainties.

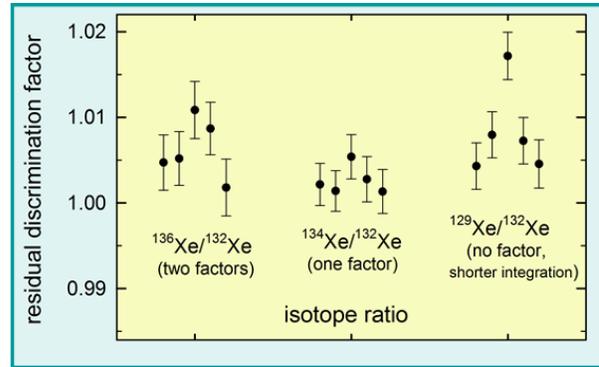


Fig. 3. Residual deviation from air composition for the five calibrations in Fig. 2 after internal calibration.

First results: First results using the instrument have been obtained on two sets of micrometeorites from Antarctica [8]. Interestingly two different characteristic patterns for the Xe isotopes were recognized, one that resembles Xe in primitive meteorites, and another which resembles mass-fractionated air [8-10].

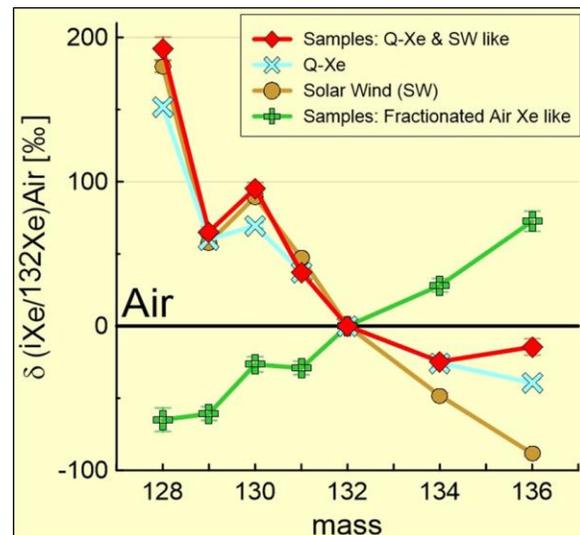


Fig. 4. Typical Xe patterns observed in micrometeorites in comparison with established Xe components (from [8]).

References: [1] Baur H. (1999) *EOS Trans. AGU*, 46, 1118. [2] Heck P. R. et al. (2007) *ApJ*, 656, 1208-1222. [3] Meier M. M. M. et al. (2012) *GCA*, 76, 147-160. [4] Crowther, S. A. et al. (2008) *J. Analytic. Atomic Spectr.*, 23, 938-947. [5] Strashnov I. and Gil-mour J. D. (2013) *Meteoritics & Planet. Sci.*, 48, 2430-2440. [6] Ott U. et al. (2010) *Meteoritics & Planet. Sci.*, 45, A58. [7] Meshik A. et al. (2014) *GCA*, 127, 326-347. [8] Baecker B. (2014) PhD thesis, University of Heidelberg. [9] Baecker B. et al. (2012), 75th Annu. Meeting Meteoritical Society, Abstract #5044. [10] Baecker B. et al. (2012), 75th Annu. Meeting Meteoritical Society, Abstract #5056.