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## **High Precision Isotopic Ratio Measurements of Krypton and Xenon**

### **Final Report**

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HIGH PRECISION ISOTOPIC RATIO MEASUREMENTS  
OF KRYPTON AND XENON

FINAL REPORT

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ABSTRACT

A study has been concluded that investigated the ability of a modern commercial mass spectrometer to provide high precision isotope ratio measurements of krypton and xenon. A VG-354 (VG Isotopes, Winsford, UK) was modified to analyze gases. Precisions of 5 ppm relative standard error of the mean or better were obtained for isotopes of 10% abundance or greater. This successful demonstration means that it will be possible to acquire an instrument with this capability with high confidence that the stringent demands on precision will be met or exceeded.

INTRODUCTION

The problem of measuring the composition of fission-product krypton or xenon in air is a challenging one. The contribution of natural krypton and xenon to these mixtures far exceeds that of the fission products themselves; this has the effect of reducing the problem to one of determining a small difference between two large numbers, a disadvantageous analytical position but one that is unavoidable in this instance.

To make a reliable measurement of a small difference between two large numbers, it is necessary to know those two large numbers to a high degree of precision. In this case, it was estimated that precisions of better than 10 ppm (standard error of the mean) would be required. The intent of this task was to evaluate a commercially available mass spectrometer (a VG 354) in this role to see if current technology was capable of such analyses. To do this required modifying the instrument, designed for analysis of solid samples, to run gases. Enough data to evaluate its performance in measuring isotope ratios of krypton and xenon would then be accumulated and recommendations for further action made.

This report summarizes our findings since our last report. A description of earlier work can be found in the report of the noble gas workshop held in Orlando, FL, in March, 1988 (J. A. Carter, "High Precision Isotope Ratio Measurements of Krypton and Xenon Using a Mass Spectrometer," Report of the Noble Gas Workshop, March 30-31, 1988, Orlando, FL, T. J. Whitaker, compiler, PNL-SA-16246 (CONF-8803142), p. 7 and Appendix B.

#### COMMENT ON STATISTICS

The precision specified was in terms of standard error of the mean. The standard error of the mean is the standard deviation divided by the square root of the number of replicate measurements. Standard deviation is defined:

$$sd = \Sigma[(x_i - \bar{x})^2/(n-1)]^{1/2}$$

where  $sd$  is the standard deviation, and  $x_i$  represents the individual values and  $\bar{x}$  the average of  $n$  replicate measurements; The standard error of the mean is then

$$std\ error = sd/n^{1/2}$$

Relative standard error of the mean is the standard error expressed as a fractional part of the measured parameter. It may be quoted as a fraction, a percent, or in ppm. To determine the standard error of the mean:

$$rel\ std\ error = (std\ error/avg)$$

It is this term that is used in our tables to define our precision. To convert to percent relative standard error or ppm relative standard error requires multiplying the relative standard error by 100 and  $10^6$ , respectively.

## EXPERIMENTAL RESULTS

We feel it important to emphasize a few of the conclusions that were mentioned in earlier progress reports. To work at the 10 ppm level of precision, there is no aspect of the experimental protocol that is unimportant. Vacuum systems must be kept scrupulously clean and various contaminants monitored. The smallest contaminant at a given mass position will make it impossible to reach the desired level of precision. We have found unidentified peaks at masses 86 and 132 particularly troublesome.

The results listed in this report are based on data collected using a commercially available gas inlet system. Our previous work had been done using an inlet system built in-house that did not have the sophistication of the one used in this work. This system is identical to the one used on VG-3001 gas mass spectrometers. It was interfaced to our VG-354 through a side port. Two expansion volumes were available with the inlet system: 2 liters and 50 ml. Most of our work was performed by expanding one or two ml of the analyte gas into the 2-liter volume. This provided a long-lived, stable ion signal, a necessity for high precision.

A baritron pressure-reading device was installed to allow measurement of the gas trapped in the expansion volume. Readings of a baritron are independent of the mass of the atoms being registered--i. e., a given pressure of a heavy gas like xenon will give readings identical to the same amount of air. Air was therefore used to calibrate the baritron, and readings established for several volumes of interest--1 standard ml, etc. One standard ml of either krypton or xenon afforded analysis times in excess of one working day and were estimated to be about ten hours. Signal strengths during this period were more than sufficient to yield precisions considerably better than the 10 ppm standard error of the mean that was our target.

We did not have the gas syringe necessary for handling volumes less than about 1 standard ml. We were able to approximate, however, 0.1 standard ml, and found that, when expanded into the 50 ml volume (rather than the 2 liter), it gave pressure readings of about 800 microns. This pressure reading is enough to give the signal intensities (about  $10^{-10}$  amps on the most abundant isotope) required for 10 ppm work. We estimate that such a sample would last about an hour, which is enough to make 100-200

replicate measurements of the isotopic composition of the gas in multi-collector mode. If the mass spectrometer were equipped with computer-controlled pockets, it should enable the analyst to analyze both krypton and xenon in the given time frame. Although it would have to be demonstrated experimentally, we are confident that 0.1 standard ml is enough sample to make measurements at the 10 ppm level on our instrument. Analysis of samples smaller than that is a matter of speculation. Should it become critical to know the abilities of our instrument in this regard, a well-defined series of experiments will be required.

It is instructive to do a few simple calculations to determine what collection efficiencies are required to analyze samples of various sizes. Overall collection efficiencies measure the number of ions collected per atom of sample and embody contributions from several sources: transport efficiency of the gas to the ionization region; ionization efficiency of the gas atoms within that region; transmission efficiency of ions through the ion source and the rest of the mass spectrometer; and the collector efficiency at converting an impinging ion to an electrical signal. To achieve the desired level of precision, we feel that it will be necessary to collect a beam of 7-volt intensity for one hour on our instrument. Our instrument has a resistor of  $10^{11}$  ohms, so the 7 volts translates to  $7 \times 10^{-11}$  amps. One ion per second represents  $1.6 \times 10^{-19}$  amps, so the total number of ions that must be collected is about  $1.6 \times 10^{12}$ . One ml of gas contains about  $2.7 \times 10^{19}$  atoms, so this represents a collection efficiency of about  $10^{-7}$ . We estimate that such samples will run for at least 10 hours, thus increasing collection efficiency to about  $10^{-6}$ . This is the same efficiency required to run 0.1 ml for one hour. Analyzing 0.01 ml would then require an efficiency of  $10^{-5}$ .

In our earlier work, calculations were made to determine the effect of applying internal calibration to the data. It was found that, if isotopes of sufficient abundance were used for the calibration ratio, substantial improvement in precision could be realized. Regrettably, however, neither krypton nor xenon has a pair of isotopes of sufficient natural abundance that can be used for this purpose. Any isotope that is a fission product is not suitable for use in this application since the validity of the calculations is dependent on exact knowledge of the value

of the reference ratio. Under these conditions, the best choice for a ratio for krypton was thus 80/82; 80 is 2.277% abundant while 82 is 11.58%. For xenon, the best choice is 129/130; 129 is 26.44% abundant and 130 is 4.08. Using these ratios for each element produced results no better than those obtained without their application, being limited by the precision of the measurements of the smaller member of the isotope pair. Using 82/83 for Kr (11.58%/11.52%) and 129/131 (26.44%/21.18%) provided substantial improvement (factors of 3 to 5), but 83-Kr and 131-Xe are fission products; these ratios thus cannot be used for internal calibration, but the results are indicative of the power of the technique.

Application of internal calibration encounters an additional complication in that "natural" krypton and xenon are not well defined. IUPAC abundances cite only one or two places after the decimal point, which is not sufficient for high-precision work. In addition, samples of the "natural" gases vary in isotopic composition. We suspect isotopic fractionation has occurred in the separation process (rather than natural variation), but this would have to be proven experimentally. Table 1 lists selected isotopic ratios from three krypton samples that all purported to be natural.

TABLE 1: Compositions of 3 Natural Kr Samples

Sample	82/84	83/84	86/84
A	0.203501	0.201834	0.303296
B	0.202829	0.201517	0.304271
C	0.203488	0.201841	0.303328

While samples A and C were similar in composition, sample B was undoubtedly different.

We should point out that these uncertainties in composition do not present an insurmountable obstacle to the application of internal calibration. To apply the technique, it would be necessary to have a sample of each gas that all parties to the experiments agreed to call the reference; its ratios would then be used to define arbitrarily the "natural" compositions for use in the calculations. Absolute accuracy would probably not be at the ppm level. Variations from the reference values would be at the ppm level, and the differences measured for samples

of unknown composition would provide a reliable and consistent measure of their fission-product content.

Another way of implementing internal calibration might be considered. It is used extensively in the nuclear community for analysis of uranium and plutonium. This would involve addition of a double spike to each sample. This spike would consist primarily of two highly enriched isotopes, enriched to the extent that each would comprise about 50% of the mixture. These should, of course, be isotopes that are not fission products. This type of analysis would double the instrument time required since measurements of composition would have to be made both before and after addition of the spike. Thus, using a double spike would require substantially more gas handling than simple analysis of the gas and probably should be considered only if the gains in precision were essential.

A series of experiments revealed that, without internal calibration, using peak-jumping and a single Faraday cup collector did not provide good enough precision; the same data processed using internal calibration with a suitable pair of isotopes for the reference ratio did meet the precision demands, but only by using isotopes of sufficient abundance for the reference ratio. This pair always included at least one isotope that was a fission product. We therefore turned to a multi-collector data-acquisition configuration. In the VG-354, the ion optics have been so configured as to create a focal plane (instead of the normal curve). A number of collectors (also called pockets) can be mounted on this plane, and the ion beams of that number of isotopes collected simultaneously. The maximum number of collectors that can be installed is nine. Our instrument has, unfortunately, only five collectors. Since, for application of internal calibration, both krypton and xenon have more than five isotopes that must be monitored, this necessitated taking data in two phases so that the intensities of all critical isotopes could be measured. This basically doubled analysis time. Table 2 shows the two data collection configurations used for each element.

TABLE 2: Collector Configurations

Pocket	1	2	3	4	5
Kr	80	81	82	83	84
Kr	82	83	84	85	86
Xe	131	132	133	134	135
Xe	132	133	134	135	136

Not all mass positions listed have isotopes of the gas in question. There was not enough travel in the pockets of our instrument to omit a mass position in a data collection scheme. It was not, for example, possible to have a configuration for Xe that collected 131, 132, 133, 134, and 136 because not enough separation could be obtained between the pockets to be used for 134 and 136. It should be pointed out that, if internal calibration is not being used, only the second configuration for krypton would be required as it would not be necessary to monitor mass 80. Mass 82 is required as a measure of the amount of natural gas present in the sample; mass 129 or 130 serves a similar function for xenon. Mass 85 for krypton will be present only as a fission product; its half-life is far too short (10.7 years) for there to be a natural contribution. It is likely to be present at the ppm level in the sample, and it is possible that this abundance will be too low to be measured by a Faraday cup detector. If this is the case, it will be necessary to use an ion-counting detector for 85-Kr. Vendors of suitable mass spectrometers provide one ion-counting detector as an option; such collectors cannot be used to form multi-collector arrays, but a single one on the ion-optical axis can be used in conjunction with multiple Faraday collectors. We point out that, if ion counting of 85-Kr is necessary, it will require a two-pass data-taking scheme for analysis of that element, one for 85-Kr and one for all the other isotopes.

We emphasize that multiple configurations used in our experiments for a single element are required solely due to the limitation imposed by our instrument's specific configuration of five collectors. More collectors (seven) would permit simultaneous collection of all isotopes of interest of one element in one pass. Complete analysis would thus require two pocket configurations, one for krypton and one for xenon. Two configurations will always be necessary because the dispersion of a mass

spectrometer varies with mass. Dispersion can be thought of as a measure of how far isotopes adjacent in mass are separated. Krypton isotopes, being lighter than xenon isotopes, will be farther apart in space than xenon's when they arrive at the spectrometer's collector plane. This necessitates different collector positions for the two elements. The positions of the individual collectors can be controlled (for a price) through digital stepping motors by the mass spectrometer's computer. Our pockets are not so controlled, requiring manual adjustment. It takes about one hour to switch the collectors manually from the configuration required for one element to that for the other. This, of course, consumes valuable sample, and would not be tolerable in an instrument dedicated to the work envisioned in this project.

Our experiments revealed that our instrument was capable of meeting the targeted precision of 10 ppm standard error of the mean for most ratios of both elements. The only exceptions were those involving isotopes of low abundance (less than about 10%), and these isotopes, except for 85-Kr, are not fission products. Table 3 presents results for krypton and Table 4 for xenon. Each value in the tables represents 100 individual measurements of the ratio in question; it required about 45 minutes to collect this amount of data. All data were taken in multi-collector mode; no internal calibration corrections have been applied. A correction for intensities measured by the axial collector was necessary and has been applied to all tables in this report. This collector is recessed behind the focal plane of the instrument to accommodate a Daly detector. Divergence of the beam after it crosses the focal plane causes this collector to intercept a smaller fraction of the beam than do the other collectors; this fraction varies with mass. The correction factor for krypton was 1.001016; for xenon (Table 4) it was 1.00075.

TABLE 3: Isotopic Ratio Results for Kr

Pocket configuration: 80 82 83 84 85

Sample	rel		rel		rel	
	80/84	std err	82/84	std err	83/84	std err
1	0.040102	0.000009	0.203405	0.000005	0.201841	0.000004
2	0.040105	0.000007	0.203421	0.000005	0.201842	0.000005
3	0.040112	0.000008	0.203436	0.000004	0.201851	0.000004
4	0.040111	0.000008	0.203432	0.000004	0.201845	0.000003
5	0.040090	0.000009	0.203402	0.000004	0.201828	0.000004

Pocket configuration: 82 83 84 85 86

Sample	rel		rel		rel	
	82/84	std err	83/84	std err	86/84	std err
1	0.203501	0.000003	0.201848	0.000004	0.303317	0.000003
2	0.203493	0.000003	0.201845	0.000004	0.303310	0.000003
3	0.203486	0.000003	0.201837	0.000004	0.303333	0.000003
4	0.203480	0.000004	0.201838	0.000003	0.303344	0.000002
5	0.203480	0.000003	0.201836	0.000004	0.303338	0.000003

TABLE 4: Isotope Ratio Results for Xe

Pocket configuration: 131 132 133 134 135

Sample	rel		rel	
	131/134	std err	132/134	std err
1	2.028862	0.000003	2.572478	0.000004
2	2.028743	0.000003	2.572346	0.000004
3	2.028736	0.000004	2.572245	0.000005

Pocket configuration: 132 133 134 135 136

Sample	rel		rel	
	132/134	std err	136/134	std err
1	2.572440	0.000003	0.850016	0.000004
2	2.572450	0.000003	0.849982	0.000004
3	2.572503	0.000005	0.849960	0.000003

Each measurement was made on a different replicate sample, with the inlet to the mass spectrometer being closed and then reopened. Some sets of data were taken the same day, but with at least an hour in between. The data for each element were thus accumulated over a period of several days and represent a realistic measure of reproducibility. Two standard milliliters were used for the sample, expanded into the two liter volume.

This gave a signal intensity of 10.1 volts for 84-Kr and 7.2 volts for 132-Xe. These high intensities are necessary to achieve the desired precisions; for Table 3, the 10 ppm mark could not have been met for 80/84 without this much signal. Internal precisions were significantly better than 10 ppm standard error of the mean for all other ratios, with only an occasional value as high as 5 ppm. External precisions were not as good, as can be seen by the range of values listed. There are many reasons why this should be, none of which are readily addressable in our present laboratory. Our instrument has always exhibited a beam less stable than specification with respect to its position. This has been attributed to temperature fluctuations in our laboratory, which can be severe over the course of a day. This is particularly true in the hot summer season, during which these data were taken. Any such instability will manifest itself in poorer precision. An additional factor that almost certainly contributed to the spread in the results is the fact that, for each element, we were operating at the maximum separation of the pockets; we have historically had trouble with the two outer pockets under these conditions. Neither of these conditions would obtain with a new instrument in a laboratory with proper temperature regulation.

Results as good as those tabulated above were obtained with samples of one standard ml except for the Kr 80/84 ratio. This ratio, however, is not one of those of crucial importance. We were not able to measure sample volumes smaller than 1 ml with the equipment on hand. We have described above the exercise we carried out for an estimated 0.1 standard ml. It should be borne in mind that the performance of our instrument with regard to sample size is not critical to the success of this project. The specific instrument on hand is not the instrument to use for routine analysis of rare gas samples. For that, a mass spectrometer designed for this purpose would give substantially enhanced performance; it is just such an instrument we recommend acquiring for this project.

## CONCLUSIONS

We have demonstrated that precisions of 10 ppm or better standard error of the mean can be obtained on critical isotopic ratios of krypton and xenon. For this work we have used our VG-354 mass spectrometer, an instrument designed to analyze solid samples and modified to accept gases. Sample sizes were one or two standard ml of the pure gas, which gave an estimated 10 hours of signal usable for measurements of this quality. We are confident that, with a few adjustments of analytical protocol, 0.1 ml would be sufficient.

## RECOMMENDATIONS

There is good reason to believe that measurements as good as, or better than, those reported here can be made on a routine basis. A mass spectrometer that was designed with this specific task in mind would undoubtedly out-perform our modified one. Inclusion of at least seven pockets is essential; that way all isotopes of each element can be monitored in single collector configurations, one for each element. Position of the pockets should be controlled by a computer so that switching between elements is automatic; manual switching, as we performed, requires an hour or so and consumes valuable sample during the operation.

We feel that the next step is to obtain such an instrument. Both VG and Finnigan-MAT (and possibly others) should be able to provide one able to out-perform our present VG. It will be crucial to that acquisition process, however, to supply the vendor with specifications that unambiguously spell out precisely what is required with regard both to hardware and to software. This is not a trivial task, and only if it is properly executed will the instrument acquired provide the desired service.



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