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Noblesse Note **NG07**

Xe multicollection

Image: Noblesse HR - Noble Gas Mass Spectrometer

Summary

- The latest 5F5M Noblesse allows Xe multicollection, with measurement of all Xe isotopes in 3 mass steps.

- Hydrocarbon interferences are resolved, and zoom optics are used to allow precise beam alignment with a fixed collector array.

- We have compared single collector and 3 step ion counting multicollection of small Xe samples (4 to 8 x 10^{-13} ccSTP ^{132}Xe). Overall time for a single analysis was the same for both methods, although single collector omitted the minor isotopes ^{124}Xe and ^{126}Xe.

- Multicollection yielded better precision than single collector in raw (uncalibrated) ratios. On average, the relative standard deviations (rsd) of the ratios ^{n}Xe/^{132}Xe were reduced by a factor of 0.67. This agrees well with a factor of 0.61 expected from consideration of numbers of ions counted.

- Uncalibrated multicollection ratios ^{n}Xe/^{132}Xe show a rsd down to 0.2% which is also the value expected from ion counting statistics, and demonstrates the stability of the multicollector.

- Multicollection is essential when the highest precision is required from small samples. The same precision cannot be achieved with a single collector, as too many ions are wasted rather than counted.

- On the other hand, if high sample throughput is required, 3-step multicollection offers little advantage over a single collector. This is because sufficient standard measurements must be obtained to adequately calibrate the multicollector, whereas single collector calibration is more efficient (just one calibration factor is required for a single collector, if we assume mass dependent fractionation).

- It is likely that larger samples may benefit from peak jumping on a single collector, if the precision becomes better than the stability of the detectors.

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Xe isotope measurements

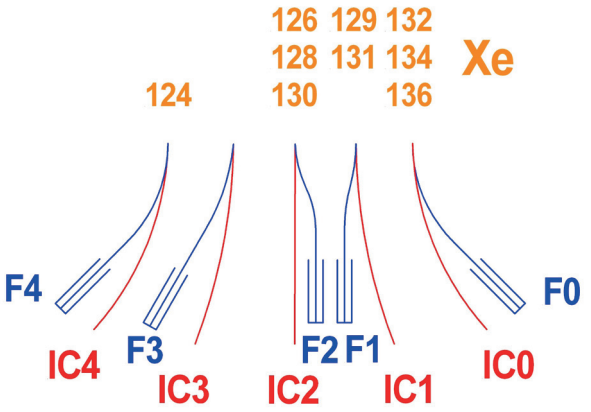
The latest 5F5M Noblesse has been used to assess Xe isotope measurement methods. Small Xe samples were measured, using both peak jumping and multicollection, and the precisions compared.

Over the course of one week, three datasets (A, B and C) were obtained, from which isotope ratio precisions could be assessed.

Dataset	^{132}Xe 10^{-13} ccSTP	^{132}Xe approx cps at t=0	Single Collector SC	Multi-collection MC	Total duration
A	4	1800	n=26	n=25	1.6 days
B	4	1800	n=30	n=30	3.2 days
C	8	3600	n=30	n=31	3.2 day

Within each series, alternate aliquots were measured using single collector and multicollection. Series B and C were run concurrently, alternating between different sample sizes, as well as between different measurement methods.

All measurements were made with discrete dynode electron multipliers. The 5F5M multicollector allowed measurement of all 9 Xe isotopes in 3 mass steps, as shown in the diagram below.



Single collector measurements used IC2, but did not include the minor isotopes ^{124}Xe and ^{126}Xe.

Examples of individual single collector and multicollector analyses are shown below.

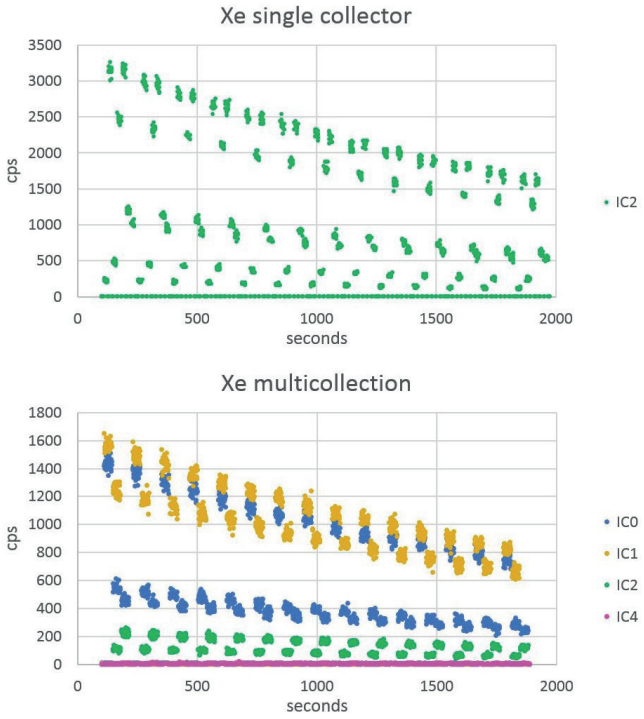


Figure 1: Examples of single collector and multicollector analysis, in the usual format of signal versus time (where t=0 corresponds to gas inlet). The signal decays as gas is removed by ionisation; roughly half the sample is consumed during the course of the analysis. The short gap at the start is due to peak centring. The overall analysis time is similar for both single collector and multicollection analyses, although any individual isotope is measured for a longer time with multicollection.

We can easily calculate how many more ions are collected using multicollection, using the information in the table below.

	Number of mass cycles	Seconds on each isotope per mass cycle	Total measurement time *for each isotope*
Single Collecor	13	13	169
Multicollection	15	30	450

Multicollection therefore counts 450/169 = 2.66 times as many ions than single collector, so the precision of the raw measurements should be better by factor √2.66 = 1.63. We return to this issue later.

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Peak Shapes

The use of zoom optics is necessary to enable exact alignment with the fixed detector array.

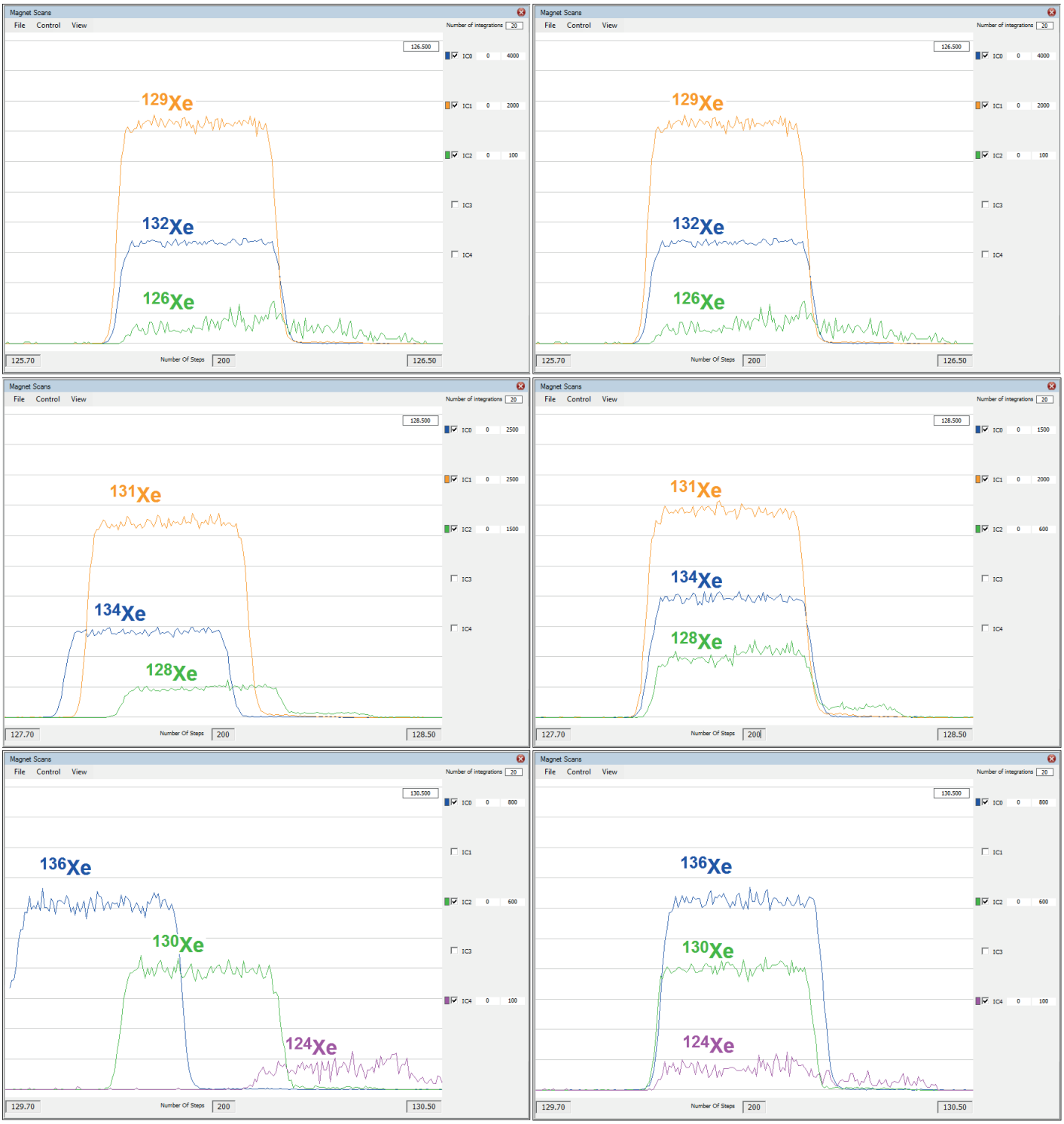

Figure 2: Peak shapes showing alignment without (left) and with (right) adjustment of the zoom optics. Hydrocarbon interferences are apparent for masses 124, 126 and 128; these can be easily resolved.

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Isotope Ratios

Isotope ratios were obtained by calculating a ratio for each cycle, which involved temporal interpolation with adjacent cycles, as even with multicollection not all isotopes were measured simultaneously. These ratios were then linearly extrapolated to gas inlet time. No further processing (e.g. to correct for detector gain variations) was applied to the data.

Isotope ratio precisions using multicollection

The plot below shows precision (reproducibility) of Xe isotope ratios obtained by multicollection, as a function of mass. Precision is given as the relative standard deviation (rsd) of the Xe isotope ratios, normalised to ^{132}Xe, for the datasets A, B and C (hence there are three points at each mass).

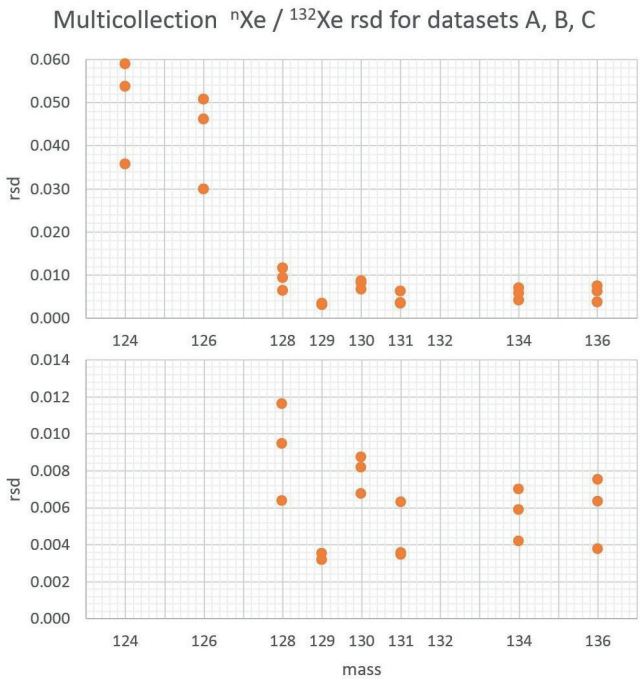

Figure 3: Relative standard deviations (rsd) of Xe isotope ratios, normalised to ^{132}Xe, for the three multicollection datasets. The precision is obviously better for the major isotopes and is better than 0.4% for ^{129}Xe/^{132}Xe and ^{131}Xe/^{132}Xe for dataset C (which used larger samples).

Comparison of multicollector and single collector data

The following plots compare the rsd of ^{n}Xe/^{132}Xe, obtained by single collector and multicollection (masses 128 to 136 only).

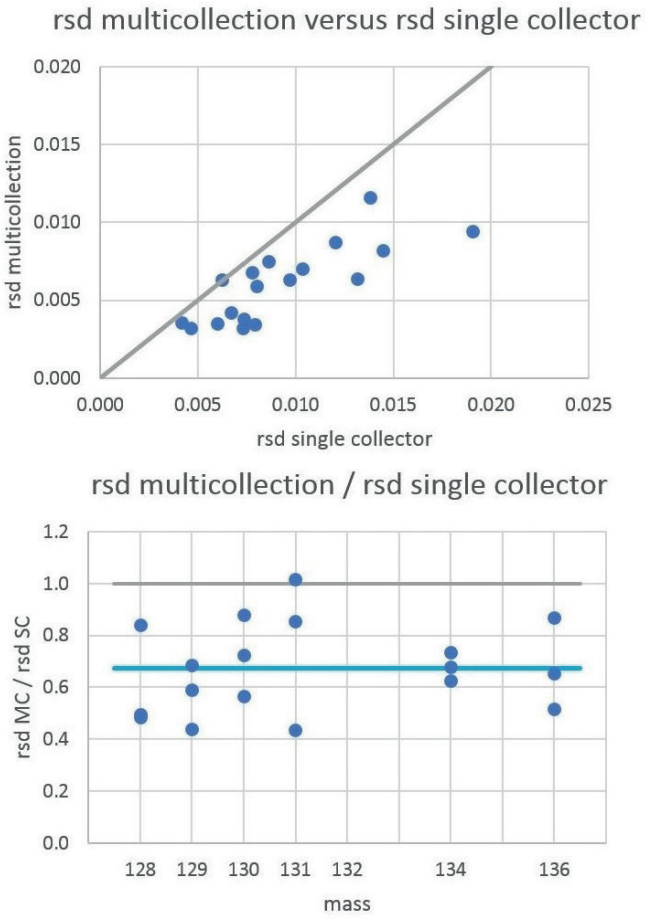

Figure 4: Comparison of precisions, shown as rsd, for single collector and multicollection data sets. On average, multicollection yields an rsd 0.67 times that for single collector peak jumping, for the same overall measurement time. This compares well with the expected improvement of 0.61. In our experiments multicollection also has the advantage of measuring ^{124}Xe and ^{126}Xe.

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Ratios from total ions counted

The results above use line fitting and extrapolation to obtain ratios at t=0, as is usually the case with noble gas analysis. Simply taking the total counts yields incorrect ratios since the signal was changing with time and measurements were not fully simultaneous.

However, in the present case, the form of the signal decay was the same in each case (since the instrument had only ever seen Xe of atmospheric composition), hence ratios calculated in this manner should still be reproducible. Furthermore, the expected rsd uncertainty for N total counts is simply $1/\sqrt{N}$, which represents the fundamental limit on information available.
We first consider the precision of ratios obtained from total counts.

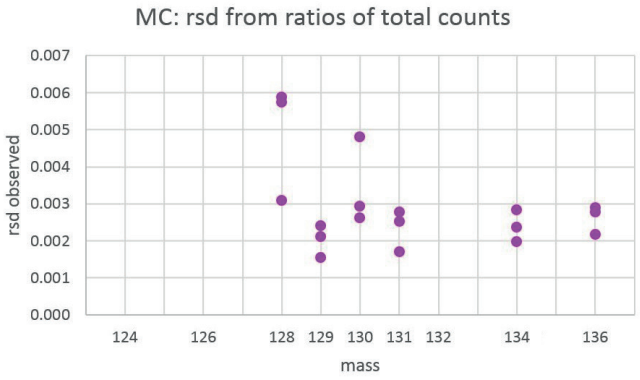

Figure 5: Precision of Xe isotope ratios from total counts, normalised to ^{132}Xe. The form of this plot is very similar to Figure 2, but the precision is better — on average by a factor of 2.0 — as we avoid the additional uncertainty introduced in extrapolating to t=0. This allows a more stringent test of the stability of the ion counting multicollector. The rsd is better than 0.2% for $^{129}Xe/^{132}Xe$ and $^{131}Xe/^{132}Xe$, for the larger samples.

Finally, we compare the RSD of ratios of means with that expected from counting statistics.

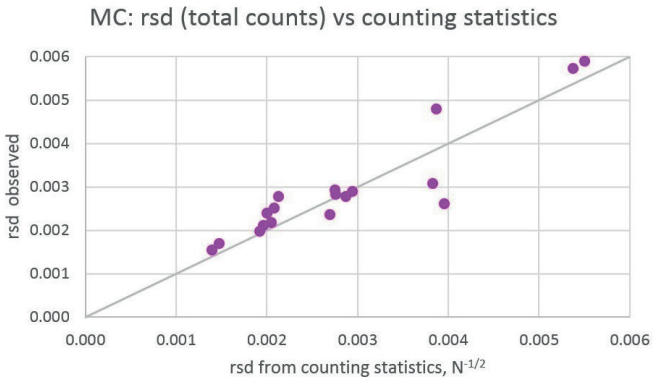

Figure 6: Ratios from mean signals: comparison of observed precision with that expected from counting statistics. There is good agreement, indicating that, at these sample sizes, counting statistics is the dominant source of uncertainty.

Figures 5 and 6 are useful as they allow a more stringent test of multicollector stability than with ratios extrapolated to t=0. They suggest that, with sufficient signal, uncalibrated ratios evaluated at t=0 could achieve a precision of 0.2% RSD.

Instrument Efficiency

It is possible to estimate the instrument transmission (or efficiency) from our data. The Xe lifetime against detection τ was 39±2 minutes. Assuming no recycling, we can write:

$$C = \varepsilon N / \tau$$

Where:

C = signal (as count rate),

N = number of atoms, and

ε = efficiency, i.e. probability of an ion generated in the source arriving at collector slits

The present experiments yield $\varepsilon = 0.43 \pm 0.02$. This can be compared with $\varepsilon = 0.67$ observed with an earlier Noblesse at Washington University in St Louis (personal communication from Professor Charles Hohenberg) and furthermore, was obtained with a resolving power sufficient to resolve hydrocarbons and C_3F_5.

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Calibration

The standard deviations discussed above — whether single collector or multicollection — all refer to raw observed ratios, i.e. without any correction for detector gains or other instrumental effects. We now consider how calibration may be performed and how this influences the overall accuracy of the results.

MC calibration

The best method of calibration will be to normalise unknown ratios to the standard, with both standard and unknown measured under the same instrumental conditions.

$$\left(\frac{^{n}Xe}{^{132}Xe}\right)_{TRUE\ x} = \frac{\left(\frac{^{n}Xe}{^{132}Xe}\right)_{TRUE\ STD}}{\left(\frac{^{n}Xe}{^{132}Xe}\right)_{OBS\ STD}} \left(\frac{^{n}Xe}{^{132}Xe}\right)_{OBS\ x}$$

This method takes into account both source and detector effects (transmission, efficiency and mass bias, although detector mass bias is likely to be negligible if the multiplier voltage is set correctly). In effect, an individual calibration factor is obtained for each isotope ratio.

If one standard is used to calibrate one unknown (both of the same size), then calibration will increase the uncertainty by a factor √2. Therefore, calibration should be performed using the average of several standards, such that the standard makes a smaller contribution to the overall uncertainty (otherwise the √2 increase on calibration largely cancels out the advantage of counting more ions). This requires sufficient time to be spent measuring standards (although the same group of standards could be used for multiple samples) and assumes that the system is stable for the duration of these experiments (i.e. that multiplier drift or aging can be ignored).

SC calibration

With a single collector, all instrumental effects are usually combined into a single parameter, called mass bias B(m), which is assumed to be a simple (often linear) function of mass m. For example

$$B(m) = [^{m}Xe/^{132}Xe]_{OBSERVED} / [^{m}Xe/^{132}Xe]_{TRUE.}$$

The following plot shows mass bias derived from our single collector measurements:

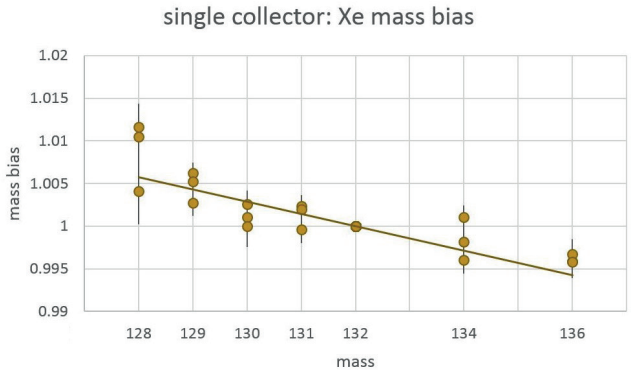

Figure 7: Instrument mass bias, as a function of mass, derived from the single collector measurements.

Consider, again, the case in which one standard is used to calibrate one similar unknown. Since the single mass bias parameter is derived from six isotope ratios at any given mass m, the uncertainty in mass bias B(m) is less than that in the ratio $^{m}Xe/^{132}Xe$ (exactly how much less will depend on mass). Hence calibration increases the uncertainties only slightly. This leads to an interesting comparison between single collector measurements and 3 step multicollection:

Single collector vs multicollection

If the highest precision for small samples is required, 3 step multicollection is essential. It is also necessary to measure sufficient standards to calibrate the detectors. A single collector yields lower precision as too many ions are wasted rather than counted; and this drawback cannot be avoided by longer calibration, nor by extending the sample measurement time (impossible as sample lifetime is limited).

By 'small samples', we mean samples similar to those measured in the experiments described here (~10^{-13} ccSTP ^{132}Xe). Larger samples should yield better precision according to counting statistics, hence precision may eventually become better than multiplier stability. Our experiments indicate that ion counting multicollection can yield uncorrected ratios to about 0.2% RSD; higher precision (possibly only for the major isotopes) may require peak jumping on a single collector.

If high sample throughput is of primary concern, then 3-step multicollection offers little advantage over single collector measurement (apart, perhaps, from measuring ^{124}Xe and ^{126}Xe). This is because if we assume mass bias is mass-dependent, single collector calibration is highly efficient: The standard measurements have to yield just one parameter, as opposed to one for each isotope ratio with multicollection.