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Investigation of the quasi-simultaneous arrival (QSA) effect on a CAMECA IMS 7f-GEO

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RATIONALE: IMS 7f-GEO isotope ratio applications increasingly involve analyses (e.g., S⁻ or O⁻ isotopes, coupled with primary ion currents <30 pA) for which quasi-simultaneous arrival (QSA) could compromise precision and accuracy of data. QSA and associated correction have been widely investigated for the CAMECA NanoSIMS instruments, but not for the IMS series.

METHODS: Sulfur and oxygen isotopic ratio experiments were performed using an electron multiplier (EM) detector, employing Cs⁺ primary ion currents of 1, 2, 5 and 11.5 pA (nominal) and a variety of secondary ion transmissions to vary QSA probability. An experiment to distinguish between QSA undercounting and purported aperture-related mass fractionation was performed using an EM for ¹⁶O⁻ and ¹⁸O⁻ plus an additional ¹⁶O⁻ measurement using a Faraday cup (FC) detector. An experiment to investigate the accuracy of the QSA correction was performed by comparing S isotopic ratios obtained using an EM with those obtained on the same sample using dual FCs.

RESULTS: The QSA effect was observed on the IMS-7f-GEO, and QSA coefficients (β) of ~0.66 were determined, in agreement with reported NanoSIMS measurements, but different from the value (0.5) predicted using Poisson statistics. Aperture-related fractionation was not sufficient to explain the difference but uncertainties in primary ion flux measurement could play a role. When QSA corrected, the isotope ratio data obtained using the EM agreed with the dual FC data, within statistical error.

CONCLUSIONS: QSA undercounting could compromise isotope ratio analyses requiring $\sim 1 \times 10^5$ counts per second for the major isotope and primary currents <20 pA. The error could be >8% for a 1 pA primary current. However, correction can be accurately applied. For instrumental mass fractionation (IMF)-corrected data, the magnitude of the error resulting from not correcting for QSA is dependent on the difference in secondary ion count rate between the unknown and standard analyses. Copyright © 2017 John Wiley & Sons, Ltd.

Secondary ion mass spectrometry (SIMS) allows for high-precision isotopic measurements at sub-micron spatial resolution using a combination of Faraday cup (FC) and electron multiplier (EM) detectors. After dead time and quantum efficiency detection corrections,^[1] EM data may still need to be corrected for the quasi-simultaneous arrival (QSA) effect. Slodzian *et al.*^[1,2] provide the theoretical framework for the QSA effect as well as experimental CAMECA NanoSIMS data that exhibit trends supporting its existence. QSA is the counterpart of quasi-simultaneous emission (QSE). The duration of the collision cascade resulting from the impact of a primary ion on a sample surface is of the order of picoseconds.^[1] If two or more ions are emitted, they may arrive at the first EM dynode quasi-simultaneously, and be registered as only one event. (The prefix “quasi-” indicates that their arrival may not literally be simultaneous, but appears simultaneous in the context of EM counting, because their separation in arrival time will be less than one thousandth of

the detector dead time.) This may result in undercounting sufficient to compromise isotope ratio data. QSA is more probable when the ratio of secondary ions to primary ions (K) is high, and is therefore likely to be observed when measuring easily ionized elements, such as S and O, in negative secondary ion mode. Although relatively small, QSA counting losses may affect IMS 7f-GEO data enough to warrant correction, depending on the ultimate precision and accuracy required. Specifically, for isotope ratio analyses requiring sub-permil precision, correction for QSA may be important, as was seen for ³⁴S/³²S isotopic ratio measurements using a NanoSIMS instrument.^[2]

The IMS 7f-GEO^[3] is a mono-collection SIMS instrument equipped with a dual Faraday cup detector system for precise isotope ratio analysis, and a single EM for detecting lower count rates. (Note that FC detectors are not affected by QSA counting losses, because the secondary ion *current*, not the number of arriving particles, is recorded.) There are certain applications, such as precise isotope ratio determination in low-abundance phases (e.g., the sulfur isotopic composition of carbonate-associated sulfate),^[4] or *in situ* pyrite micro-grain analyses^[5] requiring minimal spot size or analyte consumption, for which the use of the EM detector is preferable. It is in this context that QSA effects need to be

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considered on the 7f-GEO. Described here is a characterization of the QSA effect for isotope ratio analyses, using the EM detector on an IMS 7f-GEO instrument.

Background

Based on experimental observation and Poisson statistics, Slodzian *et al.*^[1,2] proposed a semi-empirical formula for the QSA correction of the form:

$$N_{cor} = N_{exp}(1 + \beta K_{cor}) \quad (1)$$

where N_{cor} and N_{exp} refer to the secondary ion count rates post and prior to correction, respectively. The QSA coefficient, β , should be close to 0.5 according to Poisson statistical modeling^[1] (for this reason, in earlier publications, $K_{cor}/2$ is sometimes used instead of βK_{cor}). Note that N_{exp} refers to the EM data output after dead time and detection quantum efficiency corrections,^[1] and that:

$$K_{cor} = \frac{N_{cor}}{J} \quad (2)$$

where J is the incident primary ion flux, $6.2415 \times 10^6/s$ per pA of current (for a single atomic ion such as Cs^+). For a given value of J , the relative change in count rate caused by the QSA correction is therefore βK_{cor} . Figure 1 shows the magnitude of the correction versus the primary beam current (I_p) for various N_{exp} values, assuming $\beta = 0.5$. For practical reasons, many IMS 7f-GEO applications require count rates in the region between the dotted lines. Note that it can become necessary to consider the correction for primary beam currents below 20 pA (correction of 0.8–3‰ for $1-5 \times 10^5$ counts per second at 10 pA) and it can be as high as several percent with primary currents of ~ 1 pA. Therefore, QSA counting loss is an important consideration for the analysis of elements with high ionization yield, for

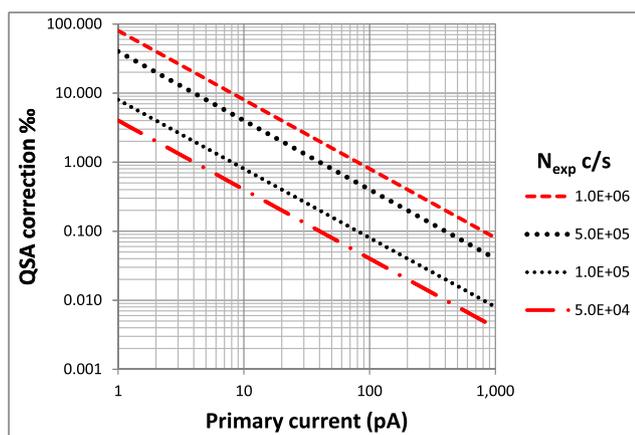


Figure 1. The theoretical permil relative change to N_{exp} caused by the QSA correction for a range of transmission conditions assuming a QSA coefficient, β , of 0.5. The change in relative correction versus primary beam current is shown for four values of N_{exp} . Because the upper limit for EM detection is 1×10^6 cps, many IMS 7f-GEO applications result in count rates between 1×10^5 and 5×10^5 cps. [Color figure can be viewed at wileyonlinelibrary.com]

which high count rates can be obtained while sputtering with low primary currents.

In practice, Eqn. (1) cannot be used directly, because K_{cor} is not known. However, defining:

$$K_{exp} = \frac{N_{exp}}{J} \quad (3)$$

from Eqns. (1) and (3) the following can be written:

$$N_{cor} = N_{exp}/(1 - \beta K_{exp}) \quad (4)$$

K_{cor} then follows from Eqns. (2), (3) and (4):

$$K_{cor} = K_{exp}/(1 - \beta K_{exp}) \quad (5)$$

For the case of the isotopic ratio, ($R = {}^{34}S/{}^{32}S$), the approach of Slodzian and others to test the QSA hypothesis was to ignore the QSA correction to the minor isotope (since it would be overwhelmed by the correction to the major isotope, which is roughly 22 times more abundant), whereby from Eqn. (1):

$$R_{exp} = R_{cor}(1 + \beta K_{cor}) \quad (6)$$

where K_{cor} is computed from the count rate of the major isotope (e.g., ${}^{32}S$) using Eqn. (5). Expanding Eqn. (6) and using delta format referenced to Vienna Canyon Diablo Troilite (VCDT),^[6] the following relationship is obtained (in units of ‰):

$$\delta^{34}S_{exp} = \delta^{34}S_{cor} + \frac{R_{cor}}{R_{VCDT}} \times \beta K_{cor} \times 1000 \quad (7)$$

This indicates that the QSA effect should be evidenced by a linear correlation between $\delta^{34}S_{exp}$ and K_{cor} . Slodzian *et al.*^[2] concluded that the linearity of the observed correlation did indicate QSA-induced undercounting of ${}^{32}S$, in general agreement with Eqn. (1). Importantly, though, despite the linear trend, the measured value of β was 0.69; not the 0.5 value predicted from Poisson statistics. Two possible explanations for this difference were suggested by Slodzian *et al.*^[2] Poisson statistics may not accurately describe the QSA phenomenon, and/or the use of different apertures to change K may cause fractionation. We will refer to the latter as “aperture-related fractionation”. Subsequently, more β determinations have been made. Table 1 is a partial list of published QSA coefficients from NanoSIMS laboratories. It is not currently understood why there is such variation in these reported values of β .

Table 1. Published QSA coefficients

Authors	Element	K_{cor}	β
Slodzian <i>et al.</i> ^[2]	S	0.025–0.2	0.69
Hillion <i>et al.</i> ^[8]	S, O	0.01–0.12	0.75
Hillion <i>et al.</i> ^[8]	C	0.005–0.075	1.0
Hillion <i>et al.</i> ^[8]	Si	0.015–0.165	0.6
Nishizawa <i>et al.</i> ^[9]	S	0.002–0.02	0.19
Zhang <i>et al.</i> ^[7]	C, Si, S	0.01–0.14	0.78

Zhang *et al.*^[7] used a more direct approach to determining β , circumventing the need for an interim calculation of K_{cor} (which inconveniently requires the starting assumption of a value for β ; typically 0.5). These authors compared N_{cor} and N_{exp} directly by measuring a single isotope and switching between EM and FC detection. They determined β to be 0.78 for C, Si and S. This is notable for two reasons. First, because it is closer to 0.69 than 0.5 (the parameter expected from Poisson statistics), confirming the observations of Slodzian *et al.* that the QSA effect did not follow Poisson statistics, and second, because it is *higher* than 0.69. This is important as Slodzian *et al.* had argued that aperture-related fractionation should have artificially increased β . Thus, if aperture-related fractionation affected the data from Slodzian *et al.*,^[2] Zhang's result should have been $0.5 \leq \beta < 0.69$ because, *a priori*, there can be no fractionation of a single isotope.

The QSA coefficient determinations listed in Table 1 were made by varying the secondary ion transmission while maintaining a constant primary beam current, as described by Slodzian *et al.*^[2] Because there should be more than one order of magnitude decrease in the QSA effect between a primary current of 1 pA and one of 20 pA (Fig. 1), for our work it was thought informative to test the QSA hypothesis for several primary currents in this range.

Sulfur isotope experiments

In order to investigate the QSA effect on the IMS 7f-GEO for S, an internal standard of pyrite ($\delta^{34}\text{S}_{\text{VCDT}} = +0.13$) was analyzed for $^{34}\text{S}^-$ and $^{32}\text{S}^-$ using Cs^+ bombardment. The nominal net impact energy was 20 keV. For these experiments, two parameters were varied: (a) the entrance slit width and (b) the primary beam current. Twenty-four

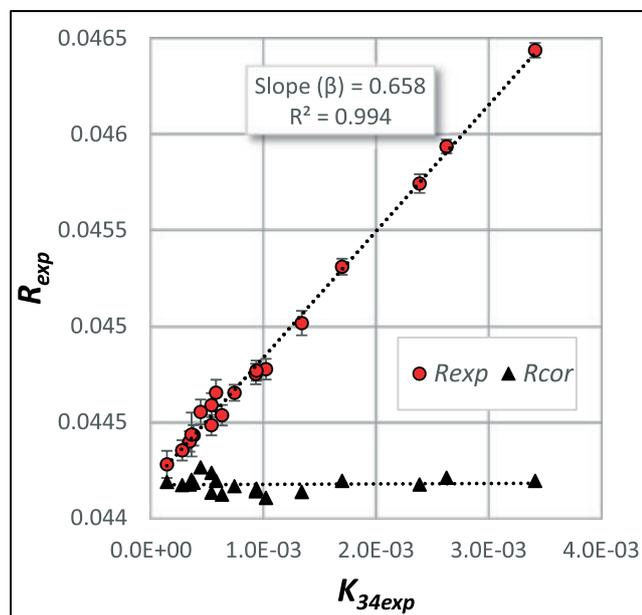


Figure 2. R_{exp} ($R = {}^{34}\text{S}/{}^{32}\text{S}$) plotted against K_{34exp} ($= N_{34exp}/I$) for results obtained using 1 pA and 5 pA primary beam currents (11.5 pA omitted for clarity). According to Eqn. (9), β is equal to the slope, 0.66. This slope was then used to calculate individual R_{cor} values (indicated by the triangles). [Color figure can be viewed at wileyonlinelibrary.com]

data sets were acquired in three sessions using eleven slit widths with 1 pA Cs^+ , eight with 5 pA and five with 11.5 pA. Magnet switching was used to collect $^{32}\text{S}^-$ and $^{34}\text{S}^-$ data using the EM detector. Individual measurements contained sufficient data cycles to achieve a precision better than 0.6‰ (1σ). Raw EM data were corrected for dead time and efficiency. The background count rate was negligible ($\ll 1$ counts per second (cps)). The approximate range in K_{cor} values was 0.004–0.1.

To examine the results, instead of using Eqn. (7) which requires an initial estimation of β to calculate K_{cor} , QSA was investigated directly from experimental data. To do this, Eqn. (6) was expanded:

$$R_{exp} = R_{cor} + R_{cor} \times \beta K_{cor} \quad (8)$$

and written as follows, since the $^{34}\text{S}^-$ correction can be ignored and K_{cor} corresponds to the major isotope, ^{32}S :

$$R_{exp} = R_{cor} + \beta K_{34exp} \quad (9)$$

According to this expression, the QSA counting loss should be indicated in a linear trend between K_{34exp} and R_{exp} , of slope β using the experimental data alone, with no intermediate step of correcting K .

Figure 2 shows the 1 pA and 5 pA data combined. The slope indicates a QSA coefficient, β , of 0.66. Individual R_{cor} values, calculated using Eqn. (9) computed after the slope (β) had been determined, are also indicated. This result is interesting: a linear QSA trend is observed and the β value is close to that obtained by Slodzian *et al.*^[2] Unfortunately, though, the result may not be very accurate, because the determination of β depends on accurate knowledge of J , the flux of Cs^+ ions striking the sample, which is required to calculate K_{34exp} . For the IMS 7f-GEO a rather large range of currents is available

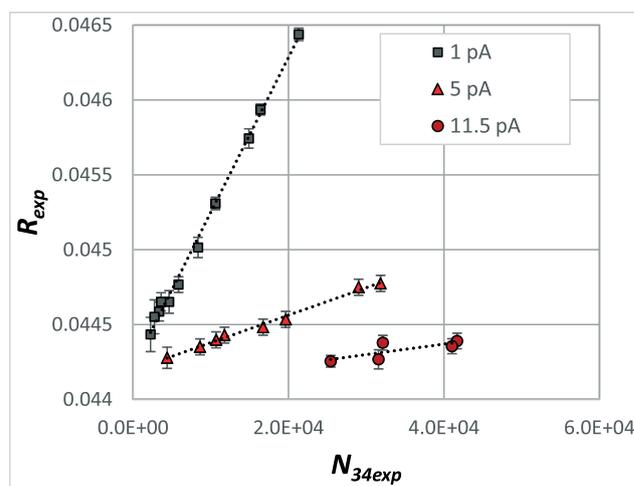


Figure 3. R_{exp} ($R = {}^{34}\text{S}/{}^{32}\text{S}$) plotted against N_{34exp} for data obtained using primary beam currents of 1 pA, 5 pA and 11.5 pA. According to Eqn. (10) each data set should have a different slope, β/I ; β being a constant and I being proportional to the primary beam current. Individual points can be corrected using the appropriate slope β/I and Eqn. (10). [Color figure can be viewed at wileyonlinelibrary.com]

(1 pA < I_p < 10 μ A), and currents are not precisely recorded below 10 pA, where the QSA effect will be most strongly manifested. (Note: the primary current was nonetheless observed to be very stable.)

For IMS 7f-GEO data it is prudent, therefore, to avoid uncertainties in J by plotting R_{exp} versus N_{34exp} , since the latter is both measured with precision and considered to have negligible QSA error.

Returning to Eqns. (3) and (9), the following can be written:

$$R_{exp} = R_{cor} + \frac{\beta}{J} \times N_{34exp} \quad (10)$$

Using this equation, data can be accurately corrected for the QSA effect without accurate knowledge of the independent values of either β , or J , using the precisely determined ratio β/J .

Figure 3 shows 1 pA, 5 pA and 11.5 pA data sets plotted in this manner. Each data set has been fitted using a linear equation in order to determine the slope β/J . These results confirm the reduction in QSA counting loss with increasing primary current, for a given range of secondary ion count rates, as discussed above and indicated in Fig. 1. The greater the slope, the greater the ultimate QSA correction, so the choice of primary beam current should be considered carefully when designing a SIMS experiment.

In Fig. 4, the 'slope values' from Fig. 3 have been plotted against $1/J$ in order to determine β , which is the slope of the line shown on the figure. Figure 4 is useful because the ordinate represents only secondary ion data and the abscissa only primary ion data, thereby graphically illustrating the dependency of the calculated slope, β , on the accuracy of the J measurement. It is notable that the three slope values, corresponding to the three primary currents, follow the trend predicted by the QSA equations, with a constant β value (≈ 0.66) common to all measurements.

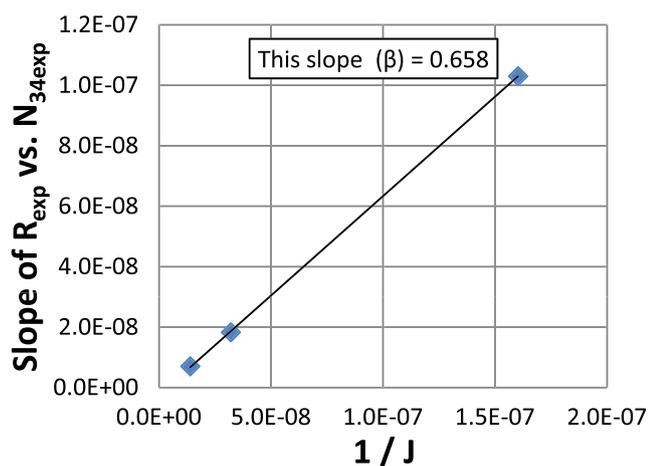


Figure 4. The three slope values from Fig. 3 plotted against $1/J$. The slope of the line in this figure is therefore β and is equal to 0.66. The ordinate represents only secondary ion data and the abscissa only primary ion data, thereby graphically illustrating the dependency of the experimentally determined β value on the accuracy of the J measurement. [Color figure can be viewed at wileyonlinelibrary.com]

Oxygen isotope experiments

A set of oxygen isotope ratio measurements was performed on a sample of Suprasil glass, using Cs^+ primary bombardment at 20 keV impact energy, as was done for the sulfur isotope measurements.

As stated above, Zhang *et al.*^[7] observed the QSA effect via sequential EM and FC detection of a single isotope (so-called single-isotope method). On the IMS 7f-GEO, a similar experiment can be performed.

Consider the ratio ($R = {}^{16}O_{FC}/{}^{16}O_{EM}$), in which the FC data have been corrected for background and yield, and the EM data have been corrected for dead time and efficiency. R has a numerator assumed to be unaffected by counting loss, and a denominator that will be affected. R would be equal to unity in the absence of any QSA counting loss; thus, $R_{cor} = 1$ whereas R_{exp} will be greater than unity when counting loss occurs. From Eqn. (6) it follows that R_{exp} is simply equal to $1 + \beta K_{cor}$, with K_{cor} being the FC counts per incident primary ion. Therefore, a plot of R_{exp} versus K_{cor} will have a slope of β , and an intercept of 1. This single-isotope method yields a QSA coefficient unaffected by aperture-related fractionation.

In contrast, Slodzian *et al.*^[2] and others have made QSA coefficient determinations using a two-isotope method, which has engendered conjecture regarding the contribution of possible aperture-related fractionation to their results. The latter can be investigated by combining the two-isotope method and the single-isotope method in the same experiment. In this way, an identical set of entrance slit widths and identical primary beam current are used for both modes. Aperture-related fractionation, if present, would cause a different value for β to be obtained via each method.

For this combined two-isotope and single-isotope experiment, ${}^{16}O^-$ and ${}^{18}O^-$ signals were recorded on the EM and an additional measurement of ${}^{16}O^-$ was made on an FC

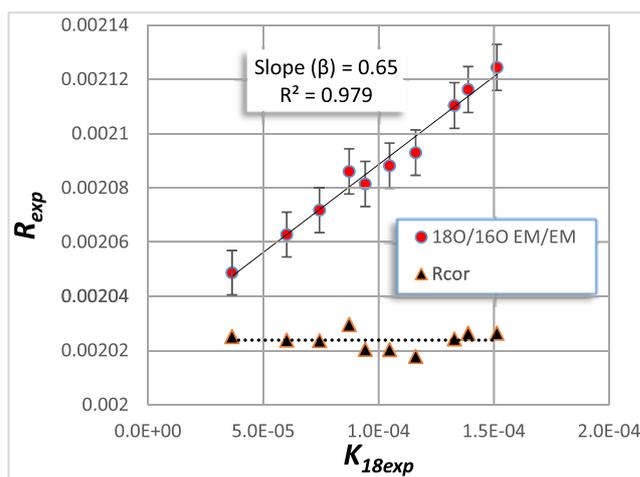


Figure 5. R_{exp} ($R = {}^{18}O/{}^{16}O$) plotted against K_{18exp} ($= N_{18exp}/J$). The EM was used for both isotopes. A linear trend is observed in accordance with Eqn. (9) (modified for oxygen isotopes), the slope indicating a QSA coefficient of $\beta = 0.65$. Using this value for β , individual data points can be QSA-corrected via Eqn. (9); the resulting R_{cor} values are indicated in the figure. [Color figure can be viewed at wileyonlinelibrary.com]

detector for each acquisition cycle. The EM data were corrected for dead time and efficiency, and the FC data were corrected for background and yield. The primary beam current was nominally 2 pA.

Two-isotope method data are shown in Fig. 5, plotted according to Eqn. (9) (modified for O isotopes), and the single-isotope method data are shown in Fig. 6. A linear trend is observed in each case and the slopes (β) are the same within error, corresponding to a coefficient value, $\beta \sim 0.65$. The effect of aperture-related fractionation therefore does not appear to be observed. (Note that although the β value of 0.65 may not be precisely constrained, the QSA correction *can* be accurately applied from the raw data via the β/J ratio, as described earlier; R_{cor} values are also plotted in Fig. 5.)

Deviation in β from expected Poisson value

If aperture-related mass fractionation is not responsible for the discrepancy between measured and theoretical QSA coefficient values, what is the explanation? Slodzian *et al.*^[2] suggested that the Poisson statistical model used was perhaps inadequate to describe the process.

This may indeed be the case, because K_{cor} is calculated using a beam of secondary ions which is initially produced by sputtering, but then subsequently attenuated by physical apertures. In other words, the ions used to calculate K_{cor} have undergone two separate processes: emission and attenuation. Thus, the resulting value of K_{cor} may not be a true Poisson random variable. For illustration, consider a single group of three quasi-simultaneously emitted ions. For a given set of aperture settings, each ion has an equal probability of passing through to the detector and 3, 2, 1 or zero ions will succeed. If zero ions reach the detector, $K_{cor} = K_{exp} = 0$. But if

1 or more ions reach the detector this is termed an 'event', and $K_{exp} = 1$, but $K_{cor} = 3, 2$ or 1. Thus, there is a potential counting loss which varies with aperture size. The type of pass-fail system that produces K_{cor} is more suitably modeled using the binomial distribution. However, such a model requires a probability distribution (i.e., probability that 0, 1, 2, 3 ... ions will be emitted per incident primary ion) as an input. Using this two-stage model, β becomes a function of the initial probability distribution, leading to predicted values $0.5 < \beta < 1$, when distributions favoring more multiple, and less single secondary ions than Poisson theory are employed.

Referring to Table 1 once more, it is noticeable that experimental β determinations are quite variable. If a model other than Poisson were applicable, it might be expected that β determinations would differ from 0.5, but still cluster around a mean value. A two-stage model, as described above, could account for some variability, e.g., if the initial QSE probability distribution was affected by sample roughness, or surface conductivity. However, the spread in experimental β values is large (0.19–1.0) and so other factors may play a role.

One such factor could be the accurate measurement of J (Fig. 4), which is crucial to the accuracy of the resulting β determination. A 30% offset in J from the true value would shift β from 0.5 to 0.65. For the IMS 7f-GEO primary FC, this could certainly be the case, as described above. It should be noted also that, although the relative yield of the secondary ion detectors is known, the relative yield between the primary and secondary detectors is not. It could be that the relative yield of the detectors used to measure N_{exp} and J is not well constrained and estimations of β will necessarily contain the corresponding uncertainty. Therefore, although J may be precisely measured, there could be fundamental parameters (e.g., primary FC background, relative yield between primary and secondary detector, etc.) which cause an instrument-to-instrument shift in $J_{measured}$ versus J_{true} .

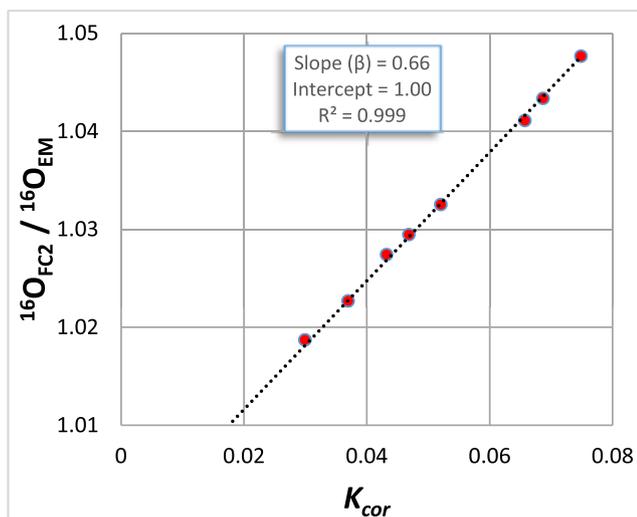


Figure 6. R_{exp} ($R = {}^{16}\text{O}_{\text{FC}}/{}^{16}\text{O}_{\text{EM}}$) plotted against K_{cor} ($= {}^{16}\text{O}_{\text{FC}}/J$). The data used for this figure and Fig. 5 were obtained in the same experiment, and thus the primary beam current and slit widths used were identical. This figure, however, contains data from only one isotope and therefore the slope cannot be affected by aperture-related fractionation. [Color figure can be viewed at wileyonlinelibrary.com]

QSA and data correction using reference standards

SIMS results are typically corrected for instrumental mass fractionation (IMF) via data acquired from a standard reference sample (S) analyzed using the same protocol as the unknown sample (U). How does the QSA correction propagate through this process? Using sulfur as an example, returning to Eqns. (3) and (4), and ignoring the QSA correction to the minor isotope, the following can be written:

$$R_{cor} = R_{exp} \left(1 - \frac{\beta}{J} \times N_{32exp} \right) \quad (11)$$

So, a QSA correction factor, C , can be defined:

$$C = 1 - \frac{\beta}{J} \times N_{32exp} \quad (12)$$

Standard and unknown will be analyzed with the same primary beam current, so J is constant and C is a function of N_{32exp} . Therefore, if the count rate differs between the standard and unknown analyses, differing QSA correction factors will ensue. The rate of change in C with N_{32exp} will be:

$$\frac{dC}{dN_{32exp}} = -\frac{\beta}{J} \quad (13)$$

and from Eqns. (12) and (13), the relative change:

$$\frac{dC}{C} = -\frac{dN_{32exp}}{\left(\frac{I}{\beta} - N_{32exp}\right)} \quad (14)$$

The net effect of the QSA correction can now be estimated by calculating the difference between the IMF-corrected $\delta^{34}\text{S}$ value calculated using QSA-corrected data from both sample and standard, and the IMF-corrected $\delta^{34}\text{S}$ value calculated completely omitting the QSA correction on both sample and standard data.

Without the QSA correction, the following can be written (in units of ‰):

$$\delta^{34}S_{imf}(no\ Q) = \left\{ \frac{R_{Uexp}}{R_{Sexp}} - 1 \right\} \times 1000 \quad (15)$$

and with QSA correction,

$$\delta^{34}S_{imf}(Q) = \left\{ \frac{(C + dC) \times R_{Uexp}}{C \times R_{Sexp}} - 1 \right\} \times 1000 \quad (16)$$

where dC is the difference in correction factor between U and S . The resulting offset can be written as:

$$\Delta q = \delta^{34}S_{imf}(Q) - \delta^{34}S_{imf}(no\ Q) \quad (17)$$

From Eqns. (15), (16) and (17) comes:

$$\Delta q = \frac{dC}{C} \times \frac{R_{Uexp}}{R_{Sexp}} \times 1000 \quad (18)$$

And from Eqns. (14) and (18):

$$\Delta q = -\frac{dN_{32exp}}{\left(\frac{I}{\beta} - N_{32exp}\right)} \times \frac{R_{Uexp}}{R_{Sexp}} \times 1000 \quad (19)$$

which, if $R_{Uexp}/R_{Sexp} \sim 1$, may be approximated thus:

$$\Delta q \approx -\frac{dN_{32exp}}{\left(\frac{I}{\beta} - N_{32exp}\right)} \times 1000 \quad (20)$$

Figure 7 is a graphical representation of this function (assuming a nominal $\beta = 0.5$, to allow for straightforward comparison with Fig. 1). For practical purposes, primary current is more informative to the SIMS analyst than J , and so Δq is plotted versus primary beam current (in this case Cs^+) for three N_{32exp} values, 5×10^4 , 5×10^5 and 1×10^6 cps, and three associated dN_{32exp} values, 5×10^4 , 1×10^5 and 2×10^5 cps. It is immediately apparent that

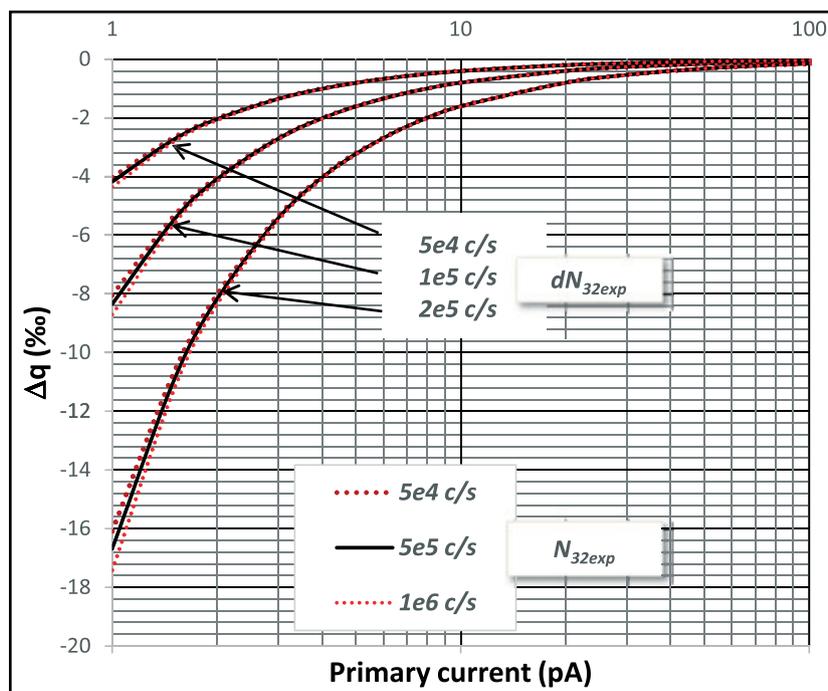


Figure 7. Δq , the difference between the IMF-corrected $\delta^{34}\text{S}$ value that has been QSA-corrected for both unknown and standard, and the IMF-corrected $\delta^{34}\text{S}$ value with no QSA correction on either unknown or standard, is plotted versus primary beam current. There are three groups of three curves. Each group corresponds to a different value of dN_{32exp} , i.e., the difference in count rate between the unknown and the standard. The curves within each group represent different N_{32exp} count rates from the standard. It is noticeable that, compared with the effect of dN_{32exp} , N_{32exp} has a minor effect on Δq . [Color figure can be viewed at wileyonlinelibrary.com]

Table 2. IMF-corrected $\delta^{34}\text{S}$ values obtained in EM/EM mode (with and without QSA correction, and corresponding Δq and dN_{32exp}) and in dual FC mode (no QSA effect)

EM/EM mode	Run 1	Run 2
$\delta_{imf}^{34}(\text{no Q})^a$	-49.5 (0.19)	-48.2 (0.27)
$\delta_{imf}^{34}(\text{Q})^a$	-48.0 (0.19)	-47.5 (0.27)
Δq^a	+1.5	+0.7
dN_{32exp}^b	-1.8×10^5	-0.8×10^5
Dual FC mode	Run 1'	Run 2'
$\delta_{imf}^{34}^a$	-47.8 (.16)	-47.6 (0.11)

Numbers in parentheses indicate the 1σ standard error for each run.
^aper mil; ^bcounts per second.

N_{32exp} has a minor effect on Δq compared with the effect of dN_{32exp} , and that Δq becomes sufficiently large to potentially compromise data for primary beam currents below 20 pA. For a primary current of 1 pA, Δq could be higher than 10‰ for larger values of dN_{32exp} . Noting that the dN_{32exp} between unknown and standard may frequently be $>2 \times 10^5$ cps, it seems prudent to correct for QSA if using primary beam currents <20 pA. (It should be noted that if using molecular ion bombardment, Fig. 7 should be adjusted according to the number of primary particles per unit charge.)

The precise isotope ratio measurement capability of the IMS 7f-GEO in dual FC mode was used to check the QSA correction. (Note: the dual FC mode has no QSA effect.) Table 2 contains illustrative results of sulfur isotope analyses performed on the same sample and using the same analytical conditions as discussed above. Two runs were made using the EM detector for measuring $^{32}\text{S}^-$ and $^{34}\text{S}^-$ (nominal $I_p = 9$ pA). After each run an additional measurement was made in the same location using the dual FC mode ($^{32}\text{S}^-$ and $^{34}\text{S}^-$ isotopes measured each in a different FC detector). A standard was also run using both modes. When the QSA correction is applied to both standard and unknown, the EM results agree with the dual FC mode, within error. When the QSA correction is not applied, the results differ by an amount related to dN_{32exp} in accordance with Eqn. (20). In other words, the EM isotope ratio data are statistically the same as the FC data if the QSA correction is applied, but not otherwise. (At this juncture it should be noted, however, that EM detectors exhibit 'ageing'; a decline in sensitivity over time, which becomes more rapid as counts rates approach 1×10^6 cps. A correction for aging can be applied, but should not be necessary if the maximum count rates are $<3 \times 10^5$ cps.)

A further ramification of omitting the QSA correction is the effect on 'external' precision, i.e., the reproducibility of repeated measurements of the same sample. For a variety of reasons the secondary ion count rate can vary with analytical location, even from a sample of uniform composition. Without the QSA correction, the apparent external precision will worsen, depending on the extent of the secondary ion count rate variation.

CONCLUSIONS

1. Sulfur and oxygen isotope ratio data sets acquired on an IMS 7f-GEO using an electron multiplier (EM) show QSA counting loss, with trends corresponding to equations derived in this paper from those first proposed by Slodzian *et al.*^[2] For applications requiring secondary ion count rates $>1 \times 10^5$ counts per second for the major isotope, the QSA correction (>0.4 permil if using primary currents <20 pA) becomes advisable for many isotope ratio applications.
2. For the IMS 7f-GEO, the isotope ratio data obtained on an EM can be accurately corrected for QSA counting loss, without independent knowledge of either β or J because, for given instrumental conditions, the parameter β/J can be accurately determined from *secondary ion* experimental data.
3. Comparison of precise isotope ratio determinations of the same sample using EM mode and dual FC mode show good agreement when the QSA correction is applied to the EM data.
4. When calibrating using a standard reference sample, the error introduced by not correcting for QSA is strongly dependent on the *difference* in secondary ion count rates between the unknown and the standard, in addition to the primary beam current. Correcting for QSA improves external precision and allows for more accurate comparison with FC measurements.
5. The QSA coefficient, β , can be estimated directly from experimental data without intermediate calculation of K_{cor} . For the IMS 7f-GEO at Washington University, β was roughly 0.66 for both S and O. Although it cannot be accurately determined because of primary ion flux uncertainty, the value is close to $\beta = 0.69$ obtained by Slodzian *et al.*^[2] This result differs from the 0.5 value derived from Poisson statistics. However, the results of a combined FC-EM single-isotope and EM-EM two-isotope experiment indicate that aperture-related fractionation does not appear to play a substantial role in the observed difference. The reason for the wide range of inter-laboratory measured β values remains unclear.

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