

Occurrence and Reduction of Noise in Inductively Coupled Plasma Mass Spectrometry for Enhanced Precision in Isotope Ratio Measurement*

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The limitations imposed upon measurement precision by instrumental noise sources present within the inductively coupled plasma mass spectrometer used have been established using noise spectral analysis. Based upon the spectral information gained, a methodology for the sequential measurement of isotopes has been developed to minimize the deleterious influence of non-random instrumental noise. Efficient use of the noise reduction techniques available within the peak-jumping mode have been found to remove the majority of the instrumental noise associated with sample introduction and excitation, facilitating a measurement precision of approximately 0.05% relative standard deviation, with respect to the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio. The precision of isotope ratios has been found to be limited by inaccuracies associated with the operation of the quadrupole mass analyser and the statistical error arising from the random arrival of ions at the detector.

Keywords: *Inductively coupled plasma mass spectrometry; noise spectral analysis; isotope ratio measurement; instrumental parameters*

The use of inductively coupled plasma mass spectrometry (ICP-MS) in isotopic ratio studies has been somewhat restricted by its failure to offer the precision and accuracy attainable by more established techniques such as thermal ionization mass spectrometry (TIMS). The precision achievable by ICP-MS, in the range 0.1–1.0% relative standard deviation (RSD) for isotope ratios, is generally regarded as being primarily limited by instrumental instability.^{1–3} Using TIMS, a precision of less than 0.005% RSD for isotopic ratios can be achieved, by use of acquisition periods of up to 24 h. A number of studies have utilized noise spectral analysis or high-speed photography to gain an understanding of the frequency characteristics and origin of instrumental noise occurring in ICP-MS.^{4–8} Noise spectral analysis has shown the noise characteristics of ICP-MS instruments to be essentially similar to those observed in inductively coupled plasma atomic emission spectrometry (ICP-AES).^{4,5} The majority of $1/f$ noise occurring in ICP-AES has been shown to arise from nebulization and vaporization processes.⁹

Several studies have addressed the optimization of instrumental parameters for accurate and precise measurement of isotopic ratios.^{1–3,6} Ting and Janghorbani³ found that many of the trends observed were the result of reducing the counting statistic, through increasing the analyte sensitivity of the ICP-MS instrument. Under optimized conditions, the precision of measured isotopic ratios has at best been 2–3 times that imposed by the counting statistics. Furuta⁶ studied the influence of dwell time per channel upon measurement precision of lead isotope ratios, in the mass scanning mode, to gain improvement *via* elimination of low-frequency noise. The detrimental influence of random, $1/f$, and discrete frequency noise upon the precision of isotope ratios required to be quantified, prior to adoption of a suitable strategy for noise reduction. In this study, the acquisition parameters available in the peak-jumping mode have been optimized, based upon noise spectral information and the nature of the residual noise investigated.

Experimental

Instrumentation

The ICP used in this study employed a 27 MHz crystal-controlled supply (Plasma-Therm, Kresson, NJ, USA, Model

HFP 2500F) with an automatic impedance-matching network. The ICP was operated at 1300 W and the outer, intermediate and carrier gas flow rates were 12.0, 0.0 and 0.75 l min^{-1} , respectively. A glass concentric nebulizer (J. E. Meinhard, Santa Cruz, CA, USA, Model TR-30-CZ), peristaltic pump (Gilson, Villiers Le Bel, France, Minipuls 2) and water-cooled spray chamber (VG Elemental, Winsford, Cheshire, UK) were used for sample introduction. The plasma source was centred about the sampling orifice, which was located approximately 12 mm above the load coil.

The quadrupole mass analyser was a VG Micromass (Altrincham, Cheshire, UK) Model 12-12S, fitted within the vacuum system of the second UK ICP-MS instrument, built on behalf of the British Geological Survey, as described previously.¹⁰ The mass resolution was set to 0.65 u, defined as the peak width at 5% of the peak height. Data acquisition was undertaken in the peak-jumping mode, with three acquisition points, each separated by 0.05 u, being allocated to each mass peak.

Noise Spectral Analysis

The collection of data was undertaken using the operating conditions utilized in isotopic ratio measurement, following an interval of at least 1 h after light-up to allow the instrument to equilibrate. The ion current from the electron multiplier (Galileo, Sturbridge, MA, USA, Model 4780V) was amplified using an operational amplifier current follower of in-house design, and low pass filtered to comply with the Nyquist sampling theorem. A sample and hold amplifier (Metrabyte, Taunton, MA, USA, SSH-4) and 12-bit analogue to digital (A/D) converter (Metrabyte DAS20) were used to digitize the analogue signal for processing by an IBM compatible personal computer. A series of ASYST 3.1 (Keithley, Rochester, NY, USA) programs were used for control of data acquisition and calculation of noise power spectra. For the collection of noise-power spectra in the range from 0 to 5 Hz, the sampling rate was 20 Hz and the –3 dB point of the in-house low pass filter, having a –12 dB per octave roll-off, was set at 10 Hz. For the collection of the 0–400 Hz spectra, the sampling rate was 1000 Hz and the –3 dB point of the in-house low pass filter, having a –30 dB per octave roll-off, was 400 Hz. In all cases 1024 data points were acquired in each data set, resulting in a frequency resolution of 0.020 Hz for the 0–5 Hz spectra,

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and 0.98 Hz for the 0–400 Hz spectra. Noise amplitude spectra were calculated by Fourier transformation, taking the sum of the squares of the real and imaginary components of the transformed data, and signal averaging in the frequency domain. For the 0–5 Hz spectra, eight sets of data were averaged, and 24 sets of data were averaged for the 0–400 Hz spectra.

Procedure for the Determination of Isotopic Ratios

There are two different modes of data collection available in ICP-MS instruments: mass scanning and peak jumping. It is the peak-jumping mode of operation that has been investigated within this study. In the peak-jumping mode, the centres of the mass peaks are sequentially transmitted by 'hopping' between selected isotopes. The acquisition method used in the peak-jumping mode is determined by a number of software definable parameters. The parameter set utilized was as follows: acquisition points per peak (three); mass step between points (0.05 u); dwell time per channel (varied); settle time between peaks (varied); number of sweeps (varied); and number of repeat integrations (10). The analyte concentrations utilized in isotope ratio analysis were 100 or 500 ng ml⁻¹ for silver and 1000 ng ml⁻¹ for lead.

Reagents

Stock solutions of silver and lead were of analytical-reagent grade. De-ionized water for the dilution of the stock solutions was obtained from a laboratory-reagent grade water system (Liquipure, Bicester, Oxfordshire, UK), generally operated at 18 MΩ. All solutions were prepared so as to contain 1% v/v HNO₃, of ultrapure reagent grade, and stored in high-density poly(propylene) bottles.

Results and Discussion

Noise Spectral Analysis

A noise-power spectrum obtained over the frequency range 0–5 Hz for ion-current monitoring of the ⁴⁰Ar⁴⁰Ar⁺ signal, at a count rate of 2×10^6 counts s⁻¹, is shown in Fig. 1(a). A 1/f noise component present below approximately 1 Hz was observed, similar to that found in ICP-AES when using a glass concentric nebulizer.¹¹ Discrete noise components were observed at 2.46 and 4.92 Hz, the latter being a harmonic of the former, for a solution uptake rate of 0.73 ml min⁻¹. These discrete noise components were absent from noise-power spectra obtained for a dry plasma. Variation of the solution uptake rate was found to cause a shift in the frequency at which these noise components occurred, as had been observed by Goudzwaard and de Loos-Vollebregt.¹² The frequency of the fundamental noise peak was observed to be equivalent to the rate at which the individual rollers on the pump head of the peristaltic pump squeezed the pump tubing.

A noise-power spectrum for ⁴⁰Ar⁴⁰Ar⁺ in the frequency range 0–400 Hz is given in Fig. 1(b). The audio-frequency (a.f.) noise at 324 Hz is a consequence of a phenomenon occurring within the ICP discharge. The origin of this phenomenon has been described as being derived from the rotation of the discharge as a consequence of non-linear flow of the plasma gas,¹¹ and also, the passage of vortex rings down the central axis of the discharge owing to the flow of plasma gas into the surrounding static air.¹³ The frequency of the a.f. noise peak was observed to vary with plasma operating conditions between 200 and 350 Hz. The influence of incident power, gas flow rates and observation height upon the frequency of the a.f. noise in the instrument used has been found to follow the trends previously reported.^{4,5} The discrete noise components occurring at 100, 150, 200, 250 and 300 Hz are all considered to be related to the discrete noise at 50 Hz owing to pick-up from a.c. power lines. Goudzwaard and de Loos-Vollebregt¹²

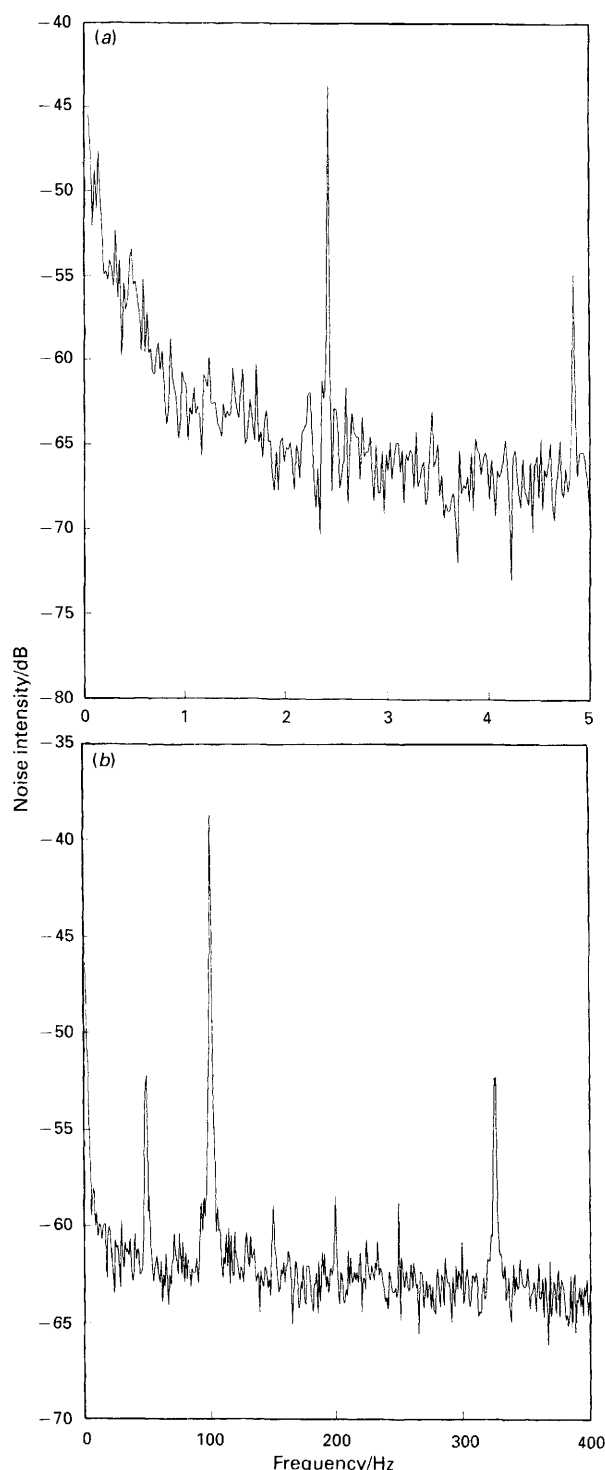


Fig. 1 Noise-power spectra for ⁴⁰Ar⁴⁰Ar⁺ ion current from the ICP-MS instrument for introduction of de-ionized water under standard operating conditions: (a) frequency range, 0–5 Hz; and (b) frequency range, 0–400 Hz

found that, in ICP-AES, the noise intensity of components occurring at 100 and 200 Hz were proportional to the square of the analyte concentration, suggesting that these are associated with signal modulation within the plasma. Noise-power spectra obtained for the ²⁰⁸Pb⁺ signal from a solution containing 1000 ng ml⁻¹ of lead were consistent with those shown in Fig. 1 for ⁴⁰Ar⁴⁰Ar⁺. Furuta *et al.*⁵ considered similar observations to imply that noise peaks are the result of a modulation of plasma ionization conditions at the sampling orifice.

The contributions of the various noise components observed

Table 1 Contribution of type of noise to overall instability

Noise type	Percentage of total instability
Random*	40
1/f	40
Frequency dependent	20

* For data collected over a period of 24 s at a count rate of approximately 2×10^6 counts s^{-1} .

in noise-power spectra can be estimated by calculating their relative contributions to the over-all instability of the ion-current signal. The RSD of a measured signal can be approximated from the mean noise level in dB (N) by use of the equation:

$$RSD = 10^{N/20} \quad (1)$$

A white noise level of between -60 and -65 dB was observed for an ion current equivalent to approximately 2×10^6 counts s^{-1} [Fig. 1(b)]. Using eqn. (1), the white noise represents an RSD of 0.06 – 0.1% , of which approximately 0.07% can be accounted for by the counting statistic. The counting statistic can therefore be considered the primary white noise source within our instrument. This limits the best possible precision attainable by isotope ratio analysis for use of a data acquisition method, which removes the detrimental influence of non-random noise. Typically, the precision observed for isotope ratio measurement by ICP-MS is 2–3 times that due to the counting statistic. Digital signal processing was utilized to determine the improvement in precision that would be attained by removing the influence of specific frequencies. This was accomplished by computing the Fourier transform of the signal and multiplying this by the desired digital filter. The inverse Fourier transform was then computed to give the filtered signal. These calculations were carried out for a number of data sets acquired under conditions identical with those used in the collection of noise-power spectra over the frequency range from 0 to 400 Hz. The improvements in precision suggest that, for the ICP-MS instrument used, the contributions of the various noise types to the over-all instability were as given in Table 1.

Isotope Ratioing

Noise spectral analysis has shown low-frequency noise to make a major contribution to the over-all instability of the ion-current signal. If the mass peaks of interest are swept rapidly, such that the time separating the measurement of isotopes is much smaller than the period of low-frequency noise, then the signal intensity can be considered unchanged and the isotopic ratio unaffected by low-frequency noise. It is the period of time that elapses between the start of measurement of the first isotope and the end of measurement of the second isotope within the ratio, referred to herein as the elapse time, which determines the range of noise frequencies removed by ratioing. The elapse time for an acquisition procedure involving a single isotopic ratio is given by:

$$\text{Elapse time} = 2 \times t_d \times n_p + t_s \quad (2)$$

where t_d is the dwell time per channel, n_p is the number of points per peak and t_s is the settle time. The use of three points per peak was adopted as this allowed monitoring of the peak profile for the measured isotopes. For noise components with periods longer than twice the elapse time, isotope ratioing will be beneficial in reducing noise, by acting as a substitute for simultaneous measurement of the isotopes, as in a multi-detector system. The improvement in measurement precision for the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio observed upon decreasing the elapse time, via the dwell time, is shown in Fig. 2. The elapse time was reduced by decreasing the dwell time per channel, of which there were three per isotope, from 81.92 to

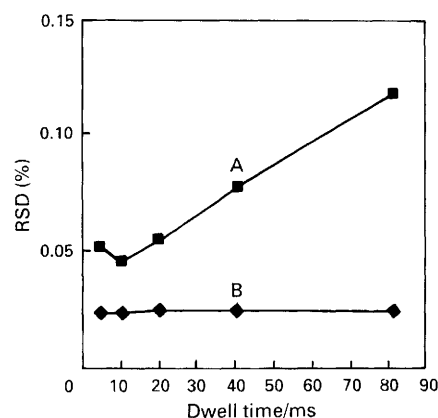


Fig. 2 Effect of dwell time on RSD for isotopic ratio measurement: A, $^{107}\text{Ag}:^{109}\text{Ag}$; and B, counting statistic. The settle time between peaks was 10 ms

5.12 ms. The integration time per isotope was held constant at 49.152 s, by increasing the number of sweeps. By retaining a fixed integration time the total ion count, and thus the counting statistic remained fairly constant. Reducing the elapse time from approximately 500 to 41 ms was beneficial to measurement precision as the detrimental influences of $1/f$ noise and peristaltic pump induced noise [Fig. 1(a)] were eliminated. Further reduction in dwell time was observed to have no appreciable influence upon measurement precision, possibly because the increase in sweep rate attained by reducing the dwell time below 5.12 ms was relatively small, while utilizing a settle time of 10 ms. It was therefore considered necessary to determine whether reduction of elapse time, by reducing the settle time, would benefit the precision. The influence of reduction in elapse time, by reducing the settle time, upon the measurement precision for the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio is shown in Fig. 3. For a dwell time of 2.56 ms, reducing the settle time from 10 to 2 ms resulted in a marginal improvement in measurement precision. Variation of the settle time within this range was observed to have no significant influence upon the accuracy of the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio. However, reducing the settle time to below 0.5 ms was found to cause a measurable change in the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio, suggesting the quadrupole mass analyser had insufficient time to stabilize following 'jumping'.

Signal Averaging

Signal averaging could be beneficial in enhancement of the signal-to-noise ratio (S/N) by reduction of any of the noise

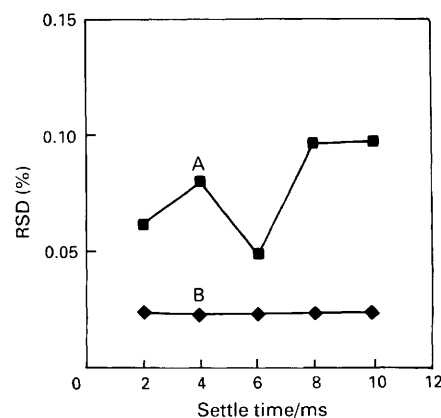


Fig. 3 Effect of settle time on RSD for isotopic ratio measurement: A, $^{107}\text{Ag}:^{109}\text{Ag}$; and B, counting statistic. The dwell time per channel was 2.56 ms

types referred to above. However, to clarify the strategy adopted herein, signal averaging will be discussed solely in terms of its effect in the reduction of non-random noise, while the reduction of random noise will be considered in terms of the signal integration period. Signal averaging of non-random noise is operational at two separate levels during data collection, these are: (i) the summation of sweeps in the multi-channel averager; (ii) the low pass filtering and anti-aliasing (preventing under-sampled high frequency components appearing at spurious low frequencies) influence of the dwell time. The summation of sweeps is an effective means of noise reduction as isotope peak profiles are added coherently in the multi-channel averager, while noise components are reduced by smoothing. The frequency of interest in the summation of sweeps is that derived from the time taken between replicate measurements of the same isotope, referred to as the cycle time. For an analysis routine in which two isotopes are monitored, to give a single isotope ratio, the cycle time is equivalent to the sum of the elapse time and the settling time, required to return from the second to first isotope. The frequency domain representation of the accumulation of sweeps is similar to that given by a comb filter whose teeth are centred at the averaging frequency and its harmonics.¹⁴ The width of the bandpass at these frequencies is given by:

$$\text{Frequency bandwidth} = 0.886/n_s \times t_c \quad (3)$$

where n_s is the number of sweeps and t_c is the cycle time. Noise frequencies outside these bandpass regions are reduced by the accumulation of sweeps. While the cycle time is somewhat fixed by the elapse time required for isotope ratioing, the number of sweeps can be increased to gain a decrease in the bandwidth of the teeth. For example, with a typical cycle time of 81 ms, and 25 sweeps, a tooth bandwidth of 0.44 Hz is obtained, however, for 500 sweeps the tooth bandwidth is reduced to 0.022 Hz. Increasing the number of sweeps accumulated, therefore, improves noise reduction at frequencies in close proximity to the averaging frequency or its harmonics. It is of course necessary to select a cycle time that does not correspond with a prominent noise component, such as that at 50 Hz owing to pick-up from a.c. power lines.

Dwell time acts as a low pass and anti-aliasing filter having a high frequency cut-off at the frequency given by twice the inverse of the dwell time. Noise at frequencies above that associated with the dwell time per channel (49 Hz for a dwell time of 20.48 ms) undergoes reduction within each channel. The dwell time is crucial in the reduction of non-random noise by both isotope ratioing and signal averaging. Decreasing the dwell time is beneficial in reduction of low frequency noise by isotope ratioing, while increasing dwell time is beneficial in reduction of high frequency noise by signal averaging. Thus, it is necessary to find a balance for dwell time to gain maximum benefit in the precision of isotopic ratios. As the instability caused by $1/f$ noise is generally more detrimental to precision in ICP-MS than high frequency noise, such as a.f. noise, it was considered best to optimize dwell time for maximum effectiveness in isotope ratioing.

Signal Integration Period

In addition to the influence accumulation of sweeps has upon non-random noise, the accumulation of sweeps is beneficial in reducing the uncertainty owing to the counting statistics. If the majority of non-random noise was removed by the combined efforts of isotope ratioing and signal averaging, the counting statistic would most probably be precision limiting. Assuming the counting statistic is limiting, the S/N should improve in proportion to the square root of the signal integration period.¹² The improvement in precision of the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio observed upon increasing the signal integration period, for an elapse time of approximately 71 ms (dwell time = 10.24 ms), is shown as a log-log plot in Fig. 4(a).

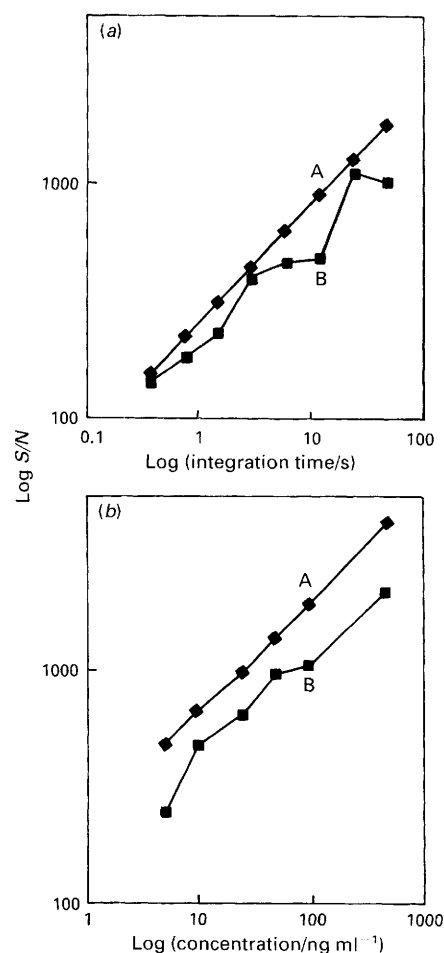


Fig. 4 Influence of non-random noise on signal-to-noise ratio (S/N) for isotopic ratio measurement. Variation in (a) isotope integration time for a solution containing 100 ng ml^{-1} of silver and (b) silver concentration for an integration time of 49.152 s. A, ^{107}Ag ; B, ^{109}Ag ; and C, counting statistic

The line representing the counting statistic has a gradient of 0.5, as is characteristic of random noise. The S/N of the isotope ratio is shown to benefit from the improvement in the S/N of the counting statistics, suggesting that the counting statistic is the limiting noise type. The improvement in precision of the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio observed upon increasing the analyte concentration, for an elapse time of approximately 133 ms (dwell time = 20.48 ms), is shown as a log-log plot in Fig. 4(b). Comparison of the rise in S/N ratio of the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio when increasing the analyte concentration and increasing the integration period shows that the full benefit of increased integrated count is not realised, as there is some divergence from the counting statistic, when the integration period is increased. This would suggest that although the counting statistic continues to be the limiting noise, an additional noise type has been introduced, which is increasing in relative intensity with integration period. It is suggested that the most probable explanation is that an increase in the signal integration period causes the significance of instrumental drift to rise, owing to prolonging of the time taken in acquisition of the ten integrations constituting a determination. That is to say, the RSD for ten integrations is influenced by change in the observed isotope ratio between integrations, arising from drift occurring incoherently in both isotopes. Hence while $1/f$ noise at frequencies above that associated with the time taken in acquisition of a single integration (2 min) is minimized, drift occurring within the 20 min period required to undertake ten such integrations is detrimental to measurement precision.

Improved Precision

The variability in measurement precision of the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio, for consecutive determinations over a 1 h 40 min period are shown in Fig. 5(a). The operating parameters utilized were: dwell time per channel = 10.24 ms; settle time = 10 ms; and number of sweeps = 1600. It was observed that although the error owing to the counting statistics remained unchanged, the precision fluctuated about a mean of approximately 0.05% RSD, suggesting the magnitude of noise varied with time. Replication of this experiment upon a VG PlasmaQuad (VG Elemental) fitted with a high-extraction interface has shown that results similar to those given in Fig. 5(a) can be obtained. However, as a consequence of the higher transportational efficiency, the reduced limitation imposed by the counting statistic for a specific analyte concentration allowed a precision approaching 0.05% RSD to be obtained at 100 ng ml^{-1} as opposed to 500 ng ml^{-1} .

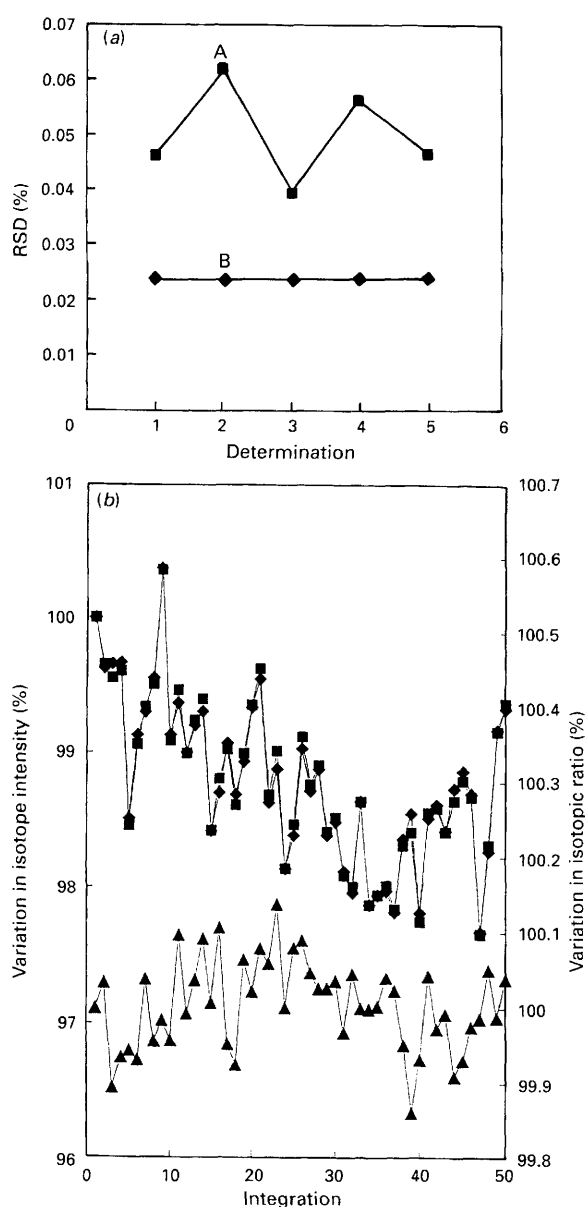


Fig. 5 Variation of silver isotope intensities and isotopic ratio over a period of 1.66 h for a solution containing 500 ng ml^{-1} of silver. (a) Five consecutive determinations, for A, $^{107}\text{Ag}:^{109}\text{Ag}$; and B, counting statistic; and (b) 50 consecutive 2 min integrations for ^{107}Ag , ^{109}Ag ; and $^{107}\text{Ag}:^{109}\text{Ag}$

Remaining Noise

The data for each of the integrations giving rise to the determinations shown in Fig. 5(a), acquired at 2 min intervals are shown in Fig. 5(b). For both the ^{107}Ag and ^{109}Ag isotopes, a long-term drift, upon which short-term fluctuations were superimposed, was observed. The long-term drift in isotope intensities is reflected in the $^{107}\text{Ag}:^{109}\text{Ag}$ isotope ratio, but in reverse. For example, a rise in the measured ratio from integration 0 to 25, and at the same time a decrease in the isotope intensities, is shown in Fig. 5(b). In addition, the isotope ratio appears to deviate from the mean value in instances for which there is notable differential change in the intensities of the two isotopes, as for integrations 3 and 39.

The results for a study of the change in the ^{206}Pb and ^{207}Pb intensities, and $^{206}\text{Pb}:^{207}\text{Pb}$ isotope ratio over a 4 h period (2 min per integration) are shown in Fig. 6. The operating parameters utilized were: dwell time per channel = 10.24 ms; settle time = 2 ms; and number of sweeps = 1600. The isotope intensities appear to have undergone significant long-term drift, both positively and negatively, during the 4 h period. The influence of this drift is prominent in the isotope ratio, causing the precision of the $^{206}\text{Pb}:^{207}\text{Pb}$ isotope ratio, averaged for the 12 determinations (one determination being the average of ten integrations), to rise to about 0.13% RSD, approximately twice the mean of the measurement precision for individual determinations.

The drift associated with the ICP ion source arises from either a change in energy transfer from the plasma to the sample, or variation in the efficiency of the sample production and transportation.¹⁵ As these should influence both isotopes coherently, the direct influence of drift associated with the ICP ion source upon the isotope ratio can, as shown above, be rendered insignificant. However, Figs. 5(b) and 6 imply that drift over a time scale of tens of minutes, or intermittent noise, unequally influencing the isotopes of interest is preventing the measurement precision of isotope ratios from being limited only by the counting statistic. It is therefore necessary to

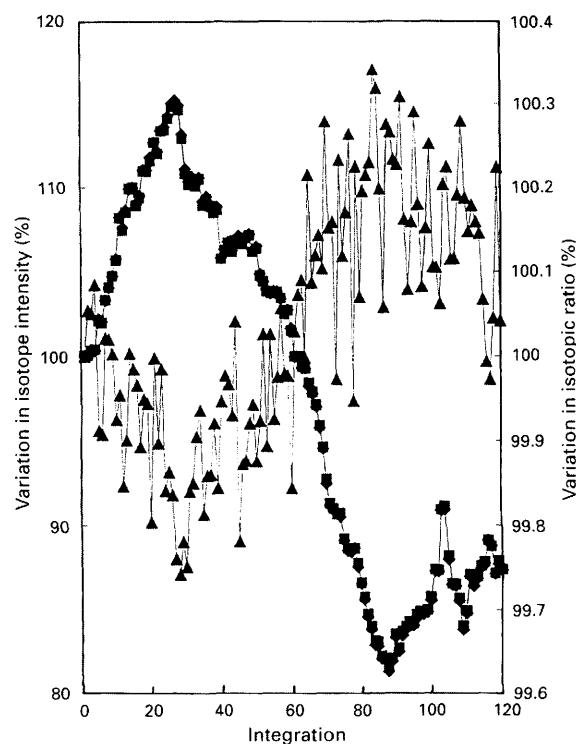


Fig. 6 Variation of ^{206}Pb , ^{207}Pb isotope intensities; and $^{206}\text{Pb}:^{207}\text{Pb}$ isotopic ratio over 120 integrations during approximately 4 h

identify the possible sources of this noise. There are two likely sources of instability associated with the mass spectrometer that have been identified. These arise from uncertainties associated with the mass bias and mass calibration of the ICP-MS instrument.

The mass bias, the deviation of the measured isotope ratio from the actual value, occurs because the sensitivity of the instrument varies with mass owing to differences in ion transmission. Generally in ICP-MS instruments, the mass bias takes the form of a loss of transmission at either end of the mass range (from lithium to uranium). Correction of mass bias within samples can be undertaken by normalizing the data to a constant, accepted ratio. It is common to use a reference standard in determination of the mass bias, however, it is necessary to assume that the measured bias remains constant during sample analysis. Russ and Bazan¹ have observed significant change in mass bias for their ICP-MS instrument (VG PlasmaQuad) over several hours.

The stability of the mass calibration [the relationship between measured mass, represented by the digital to analogue (D/A) converter channel number, and actual mass] is generally limited by the constancy of the ratio of the d.c. voltage to the radiofrequency (r.f.) voltage applied to the quadrupole rod pairs.¹⁶ For instance, a change of the order of 0.05% in the r.f. voltage amplitude, for 100 u, would cause a shift of about 0.05 u. The daily shift in mass calibration for quadrupole mass spectrometers is typically less than ± 0.02 u, however, ambient temperature change could cause additional shift.¹⁶ As the resolution of the quadrupole mass analyser is inversely proportional to the ratio of the d.c. voltage to the r.f. voltage, any shift in mass calibration caused by a change in this ratio would also be reflected in the peak shape. In combination, mass shift and resolution change may cause drift which occurs incoherently between isotopes. The nature of both mass bias and mass calibration is such that the significance of the associated instabilities would rise from middle mass (silver) to high mass (lead).

In an attempt to quantify the noise arising from instability of mass bias and mass calibration, a number of consecutive determinations were undertaken, for a fixed m/z ratio at the centre of the ²⁰⁶Pb isotope peak, using the acquisition procedure utilized in measurement of the ²⁰⁶Pb:²⁰⁷Pb isotope ratio. By monitoring ²⁰⁶Pb in both isotope channels, without 'jumping' the quadrupole mass analyser, noise coherent to both isotopes was passed into the isotope intensities and their ratio as before. However, incoherent noise arising from the mass spectrometer would have been eliminated. The accuracy [0.9999 ± 0.0002 ($n=5$)] and precision (0.032–0.041% RSD) for the measured isotope ratio was found to be limited only by the counting statistic (0.034–0.037% RSD). The mean difference between the measured precision and the counting statistic is only 0.003%. Therefore, it is suggested that the mass spectrometer and/or its associated ion optics are the source of non-random noise observed in the isotope ratio measurements reported above.

Conclusions

This study has shown that educated selection of acquisition parameters can give rise to a practical precision of about 0.05% RSD for the ¹⁰⁷Ag:¹⁰⁹Ag isotope ratio. Rapid isotope ratioing was successful in eliminating low frequency noise associated with plasma and sample introduction processes. The benefits of signal averaging were to: (i) reduce the influence of noise occurring at frequencies that did not correspond with the bandpass frequencies of the equivalent comb filter; and (ii) reduce noise occurring at frequencies above twice that associated with the dwell time per channel. Having reduced the influence of non-random noise, improved precision was obtained by reducing the counting statistic *via* increased integration time. Under optimized conditions, instabilities associated with the mass bias and mass calibration were found to impose limitations upon the accuracy and precision of isotope ratio measurements. Various methods of data processing mass spectra to minimize the uncertainties arising from the mass bias and mass calibration are currently undergoing assessment.

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