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Transient signal isotope analysis using multicollection of ion beams with Faraday cups equipped with $10^{12}$ Ω and $10^{11}$ Ω feedback resistors.

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KEYWORDS

Isotope ratio, transient signal, $10^{12}$ Ω amplifiers, $10^{11}$ Ω, signal drift, signal attenuation, hyphenation, chromatography, laser ablation, Faraday, MC-ICPMS, time lag
Abstract

To improve the precision of isotope analyses on low ion intensities using Faraday detection system, amplifiers equipped with $10^{12}$ Ω resistors (hereafter $10^{12}$ Ω amplifiers) have been developed. While the behavior of these amplifiers for steady signals has been well investigated, there is not ample evidence regarding the use of $10^{12}$ Ω amplifiers for transient signal acquisition. In this work, we investigated the simultaneous use of amplifiers equipped with $10^{12}$ Ω and $10^{11}$ Ω resistors for transient signal acquisition. Using the equation describing the relationship between the input ion current and the output voltage in the amplifiers, we showed how the transient signal duration influences the accuracy of the isotope ratio measurements. In particular, lead transient signals were investigated using the Neptune Plus MC-ICPMS and $^{204}$Pb and $^{206}$Pb isotopes were measured using $10^{12}$ Ω and $10^{11}$ Ω amplifiers, respectively. $^{204}$Pb/$^{206}$Pb isotope ratio showed an important drift due to the large time lag between $10^{12}$ Ω and $10^{11}$ Ω amplifiers. The time lag was quantified (0.175(3) s) and the isotopic drift was corrected using a method of internal signal synchronization. The $^{204}$Pb/$^{206}$Pb drift corrected data obtained from the $10^{12}$ Ω - $10^{11}$ Ω amplifier configuration were compared to the data obtained from $10^{11}$ Ω - $10^{11}$ Ω amplifiers. Our results point out that for low transient signal intensities ($<10^{13}$ A), the use of $10^{12}$ Ω - $10^{11}$ Ω amplifiers is more beneficial in terms of isotope ratio uncertainty, repeatability and trueness, compared to the $10^{11}$ Ω - $10^{11}$ Ω amplifier configuration.
1 Introduction

Transient signal isotope analysis using Multi Collection Inductively Coupled Plasma Mass Spectrometry (MC-ICP MS) has become an emerging field in isotope analytical chemistry. Various introduction systems have been coupled to the MC-ICPMS and the most commonly used hyphenation techniques are: Laser Ablation (LA)\(^1\), Liquid Chromatography (LC)\(^2, 3\), Gas Chromatography (GC)\(^4\) and Gold Trap (GT)\(^5\). The online coupling between these sample introduction systems and the MC-ICPMS generates signals with time-dependent isotope intensities. Transient isotope signals have durations varying generally from a few seconds to a few minutes and isotope ratios must be accurately measured within these time windows.

Soon after the first appearance of hyphenated techniques between the MC-ICPMS and different introduction systems, a systematic isotopic drift during isotope signal acquisition was revealed\(^1, 2, 4, 6-8\). For most transient signals, the amplifier’s time response (time constant, \(\tau\)) is slow compared to the input ion signal time variation. However, the real cause of the isotope drift is the short time lags between the time constants of the amplifiers involved in Faraday multicollection\(^9, 10\). For transient signals with durations varying from a few seconds to some minutes, the development of a new detection system with faster time response in order to overcome the isotope ratio drift is not needed. Time response synchronization of amplifiers equipped with 10\(^{11}\) \(\Omega\) feedback resistors, electronically or with post data treatment methods\(^9\), can correct this drift.

Recently, measurements of low ion intensities have been extended using Faraday detection systems with amplifiers equipped with 10\(^{12}\) \(\Omega\) resistors in the feedback loop\(^11\) (10\(^{12}\) amplifiers hereafter). While 10\(^{12}\) \(\Omega\) amplifiers provide 10 times higher voltage compared to 10\(^{11}\) \(\Omega\) amplifiers for a given ion beam, the noise level (Johnson noise) of the resistor only increases by a factor of \(\sqrt{10}\). Therefore, a theoretical 3-fold improvement in signal to noise ratio is expected but in practice this ratio improves only by a factor of two\(^12\). While most literature-documented amplifiers using 10\(^{12}\) \(\Omega\) resistors are from Thermo Fisher Scientific, other constructors propose similar developments\(^13-15\).
10^{12} \, \Omega \text{ amplifiers have been successfully used in multicollection Thermal Ionisation Mass Spectrometry (TIMS) and MC-ICPMS, either with 10^{12} \, \Omega \text{ amplifiers}^{16, 17} \text{ only, or combined with } 10^{11} \, \Omega \text{ amplifiers}^{18-21} \text{ or even with } 10^{11} \, \Omega \text{ and } 10^{10} \, \Omega \text{ amplifiers}^{22}.

Due to the quite slow time response, 10^{12} \, \Omega \text{ amplifiers have not yet been used for transient signal acquisition. We present a first approach to evaluate the potential use of } 10^{12} \, \Omega \text{ amplifiers for transient signal isotope analysis. Our study focuses on transient signal multicollection with a combination of } 10^{12} \, \Omega \text{ and } 10^{11} \, \Omega \text{ amplifiers which induces a theoretical large time shift (} \Delta t \approx 0.2 \text{ s}) between the isotope output signals. This work investigates large transient signals (~ 50 s), with chromatographic peak shape, generated by a Flow Injection system. Parameters like isotope ratio drift, uncertainty, repeatability and trueness^{23, 24} \text{ are evaluated and discussed.}

### 2 Materials and methods

#### 2.1 Instrumentation

The Neptune Plus MC-ICPMS (Thermo Scientific, Germany) used in this work has been recently installed at the Institut de Physique du Globe de Paris (IPGP). The Neptune Plus offers increased sensitivity due to a high performance interface pump combined with Jet-sampler and H-skimmer cones. The detection system is equipped with ion counting systems for small ion beams and ten Faraday cups; seven attached to amplifiers with 10^{11} \, \Omega \text{ resistors (dynamic range from 0 to 50 V) and three attached to amplifiers with } 10^{12} \, \Omega \text{ resistors (recommended range } < 0.1 \text{ V)}^{17}. \text{ In this work, signals are reported relative to } 10^{11} \, \Omega \text{ resistors. All measurements were performed in static multi-collection mode with Faraday cups. Thermo’s virtual amplifier system}^{25} \text{ was used for assigning } 10^{11} \, \Omega \text{ and } 10^{12} \, \Omega \text{ amplifiers to L1 cup (} ^{204}\text{Pb}) (\text{Table 2}). \text{ The gains of the amplifiers were calibrated daily before the analytical session and after each Faraday-amplifier re-assignation. The reproducibility of } 10^{11} \, \Omega \text{ and } 10^{12} \, \Omega \text{ amplifier gain was found to be better than 10 ppm per day. All amplifiers were set for compensation of signal decay (} \tau \text{ correction) according to the procedure recommended by the manufacturer}^{26}. \text{ For lead isotope ratio measurements, although Hg is not present in the standard solution, intensities of } m/q \approx 202 \text{ were monitored for possible } ^{204}\text{Hg isobaric interference corrections and were found to be negligible (<}10^{-4} \text{ V).}
A Flow Injection system (FI) directly coupled to a tandem cyclone-Scott type spray chamber SIS (Stable Introduction System, Thermo Scientific) with a PFA nebulizer (ESI, USA) was used as the introduction system.

The flow injection system consists of a six-way high flow valve (FAST, ESI, USA) with an injection loop of 2.4 µL and a peristaltic pump, which ensures the continuous flow of the carrier solution (HNO₃ 0.5 mol/L) at a rate of 50 µL min⁻¹. All signals were acquired with an integration time of 0.5 s. Cup configuration for Pb measurements and MC-ICPMS operating conditions are summarized in table 1 and 2.

### 2.2 Reagents

All sample dilutions were performed with 0.5 mol/L nitric acid obtained from sub-boiled 14 M nitric acid (EVAPOCLEAN system, Analab, France) and de-ionized water (Milli Q system, Millipore, Milford, MA, USA). The same acid was also used as carrier solution for the flow injection. For all Pb injections, the standard reference material SRM981 (NIST, USA) was used. For the data treatment, the re-evaluated by Doucelance and Manhès²⁷ isotope ratio values of the SRM981 were used: $^{208}\text{Pb} / ^{206}\text{Pb} = 2.1681$, $^{207}\text{Pb} / ^{206}\text{Pb} = 0.914970(17)$, $^{204}\text{Pb} / ^{206}\text{Pb} = 0.059019(5)$.

### 3 Results and discussion

#### 3.1 Evaluation of signal attenuation in amplifiers equipped with $10^{12}$ Ω and $10^{11}$ Ω resistors

Figure 1 shows a simplified representation of the amplification circuit which is associated to the Faraday cup of the Neptune MC-ICPMS. Each incoming singly charged positive ion is neutralized with exactly one electron from the Faraday cup. The electron flux in the Faraday cup is then converted to a voltage by an operational amplifier with a high-ohmic feedback resistor. For instance, if using a $10^{11}$ Ω feedback resistor, an entrance ion signal $I$ of 10 pA generates an output voltage $V_{out}$ of 1 V.
Although amplifiers used by the Faraday cup detectors are stable over a wide range of operating conditions, certain precautions must be met in order to achieve the desired pulse response when a large feedback resistor is used. For this reason a capacitor is added around the feedback resistor. This low-pass filter limits the bandwidth of the amplifier by attenuating the input ion signals with frequencies higher than the cut-off frequency of the filter.

Signal attenuation through this circuit depends both on Resistor – Capacitor (RC) time constant (τ) and on signal frequency.

The first order time constant (τ = RC) for the Neptune’s amplifier systems using 10^{11} Ω and 10^{12} Ω resistors are ~0.1 s and ~0.3 s, respectively. In the case of transient signals generated from hyphenation techniques described above, the signal frequency is expressed through the time width of the signal.

Simultaneous use of 10^{11} Ω and 10^{12} Ω amplifiers for transient signal acquisition not only generates an important isotope drift due to the large time lag (Δτ ~ 0.2 s), but may also non-uniformly attenuate signal intensities.

For studying the influence of the low-pass filter on transient signal attenuation, we need to establish the relationship between the input ion current and the output voltage. We consider an ideal operational amplifier (Figure 1) where \( I \) is the input ion current, \( I_1 \) and \( I_2 \) the currents flowing into the capacitor and resistor, respectively. According to Kirchhoff’s current law \( I = I_1 + I_2 \). By replacing \( I_1 \) by \(-CdV_{out}/dt\) and \( I_2 \) by \(-V_{out}/R\), the relationship between the input ion current and the output voltage can be obtained from the equation:

\[
\frac{dV_{out}}{dt} = -\frac{1}{\tau}(IR + V_{out}) \quad (1)
\]

where \( I, V_{out}, \tau, R \), are the input ion current, the output voltage, the amplifier first order time constant (\( \tau = RC \), \( C \) being the capacity) and the resistor, respectively. The negative sign indicates that the inverting amplifier generates a 180° phase shift from the filter input to the output.
In order to simulate an input ion transient signal \( I \) a Log-normal function (2) can be used. The Log-normal function is a good approximation of the transient signals presented in this work.

\[
I(t) = h \times \exp\left[-\left(\frac{\ln(t / t_{\text{apex}})}{w}\right)^2\right] \tag{2}
\]

where \( h, t_{\text{apex}} \) and \( w \), are parameters corresponding to, amplitude, time of maximum signal and peak width of the peak respectively.

Equation 1 was numerically solved for two time constants \( \tau_1=0.1 \) s and \( \tau_2=0.3 \) s, (corresponding to \( 10^{11} \) \( \Omega \) and \( 10^{12} \) \( \Omega \) amplifiers, respectively), and for different peak widths \( w \) of the input signal. The \( h \) and \( t_{\text{apex}} \) parameters of equation 2 have been kept constant. The aim was to simulate signal attenuation as a function of the peak width (calculated at 10 % of the signal \( I_{\text{max}} \)).

This calculation indicates how the signal attenuation in \( 10^{12} \) \( \Omega \) and \( 10^{11} \) \( \Omega \) amplifiers is related to the transient signal width. It also defines the bias for the isotopic ratio calculated from the attenuated output signals. Figure 2 illustrates the percentage of output signal attenuation according to the peak width of the transient signal. The percentage of attenuation is calculated as the ratio between the \( V_{\text{out}} \) maximum signal from equation 1 and the potential \( V \) obtained from \( I_{\max}R \), where \( I_{\max} \) is the maximum input ion intensity from equation 2 (\( I_{\max}R \) represents the potential we should measure for a continuous ion signal with an intensity \( I_{\max} \)).

For peak widths smaller than 10 s, the \( 10^{12} \) \( \Omega \) amplifier strongly attenuates the output signal compared to the \( 10^{11} \) \( \Omega \) amplifier. In contrast, for peak widths larger than 40 s, signal attenuations are significantly smaller. In the same figure, we also plot the ratios of the attenuated signals for both \( 10^{12} \Omega / 10^{11} \Omega (\Delta \tau = 0.2 \text{ s}) \) and \( 10^{11} \Omega / 10^{11} \Omega (\Delta \tau = 0.006 \text{ s}) \) amplifiers. It is obvious that for accurate isotope ratio measurements to be attained, signal ratio attenuation between the amplifiers must be 1. For \( 10^{12} \) \( \Omega \) - \( 10^{11} \) \( \Omega \) amplifier configuration, the isotopic bias is less than \( 10^{-3} \) for transient signal longer than 30 s (Figure 2). In contrast, for the \( 10^{11} \) \( \Omega \) - \( 10^{11} \) \( \Omega \) amplifier configuration, the same isotopic bias is observed for a transient signal longer than 3 s (Figure 2).
Consequently, the signal synchronization method which has been proposed in a recent work\(^9\), corrects the isotopic drift due to the time lag between the amplifiers, but not the isotopic bias due to non-uniform attenuation of the output signals. However, this approach is totally effective, when taking into account the minimum durations of transient signals as defined above.

3.2 FI-MC-ICPMS transient signals with simultaneous use of \(10^{11}\ \Omega\) and \(10^{12}\ \Omega\) amplifiers

Lead transient signals were investigated using the Neptune Plus MC-ICPMS. The main purpose was to explore the feasibility of simultaneous transient ion signal acquisition with \(10^{11}\ \Omega\) and \(10^{12}\ \Omega\) amplifiers and to compare the performances of \(10^{11}\ \Omega - 10^{11}\ \Omega\) and \(10^{12}\ \Omega - 10^{11}\ \Omega\) amplifier configurations. Transient signals were generated with a flow injection system in order to discount any possible isotope fractionation due to the introduction system (LC, GC, LA...) and therefore to investigate the isotopic drifts coming from the time lag between the amplifiers. Transient signals durations were adjusted to ~ 50 s (at 10 % of signal max) (Fig. 3).

Ten independent injections of Pb SRM981 10 ng / g (ppb hereafter) were performed: five using solely \(10^{11}\ \Omega\) amplifiers for all lead isotopes, and five with the Faraday cup of \(^{204}\text{Pb}\) isotope assigned to a \(10^{12}\ \Omega\) amplifier. All \(10^{11}\ \Omega\) amplifiers that have been chosen had similar time responses (\(\Delta \tau < 0.001\) s, isotopic drift \(<\) analytical precision) and only the simultaneous use of \(10^{11}\ \Omega\) and \(10^{12}\ \Omega\) amplifiers presented an important time lag. The same procedure was repeated for a 50 ppb concentration of Pb SRM981, in order to evaluate the influence of higher signal intensities on \(10^{12}\ \Omega\) amplifiers.

Transient signal profiles at the same lead concentration were reproducible in peak-shape and maximum intensity.

\(^{208}\text{Pb/^{206}\text{Pb}}, \ ^{207}\text{Pb/^{206}\text{Pb}}\) and \(^{204}\text{Pb/^{206}\text{Pb}}\) isotope ratios were investigated and only the \(^{204}\text{Pb/^{206}\text{Pb}}\) ratio showed an important drift when \(^{204}\text{Pb}\) Faraday cup was assigned to \(10^{12}\ \Omega\) amplifier (Figure 3a and 3c). Raw point-by-point \(^{204}\text{Pb/^{206}\text{Pb}}\) isotope ratios showed a systematic increase of about 4 % with time over a period of ~30 s.
In the case where the $^{204}$Pb isotope was detected with a $10^{11}$ Ω amplifier no drift for the $^{204}$Pb/$^{206}$Pb ratio was observed (Figure 3b and 3d).

For the correction of the $^{204}$Pb/$^{206}$Pb isotope ratio drift, the method of internal signal synchronization was used. The slope model was applied over a specific time zone (Fig. 3, segments within dashed lines) in which the measured isotope ratios showed a steady trend, avoiding high isotope ratio noisy and spiky behavior (Fig. 3).

This zone corresponds to $^{204}$Pb intensities higher than $\sim 2 \times 10^{-3}$ V and $\sim 5 \times 10^{-3}$ V for 10 ppb and 50 ppb Pb SRM981, respectively. The same zone was used for the calculation of the Relative Standard Deviation (RSD) for $^{204}$Pb/$^{206}$Pb ratio. Signals of the $10^{12}$ Ω amplifier are reported relative to the intensity on the $10^{11}$ Ω resistors.

After slope model minimization, the time lag (time shift between $^{204}$Pb and $^{206}$Pb signals) between the $10^{11}$ Ω and $10^{12}$ Ω amplifiers involved in $^{204}$Pb and $^{206}$Pb multi-collection was found to be 0.174(18) s and 0.175(3) s for 10 ppb and 50 ppb SRM981 respectively. Uncertainties were calculated as the standard deviation of the time lags obtained for five injections and were expressed for a coverage factor $k = 2$. As expected, this time lag is much higher compared to typical time lag values of $\sim 0.006$ s for $10^{11}$ Ω amplifiers.

The drift-corrected $^{204}$Pb/$^{206}$Pb ratios were then calculated using the time lag values for each injection, according to the method of internal signal synchronization.

For low $^{204}$Pb signals ($\sim 6 \times 10^{-3}$ V) the use of the $10^{12}$ Ω amplifier after isotope drift correction provides much more precise isotope ratio measurements compared to the $10^{11}$ Ω amplifier. The internal precision (% RSD) of the drift corrected $^{204}$Pb/$^{206}$Pb ratios for the $10^{12}$ Ω - $10^{11}$ Ω configuration, was found to be three times better than the precision obtained using solely $10^{11}$ Ω amplifiers (Fig. 3a and b). In contrast, % RSD of the drift uncorrected $^{204}$Pb/$^{206}$Pb ratios was similar to the % RSD for the $10^{11}$ Ω - $10^{11}$ Ω configuration.

For higher $^{204}$Pb signals ($\sim 30 \times 10^{-3}$ V), quasi similar performances were achieved between the drift corrected $10^{12}$ Ω - $10^{11}$ Ω and $10^{11}$ Ω - $10^{11}$ Ω amplifier configurations for $^{204}$Pb/$^{206}$Pb isotope measurements in terms of internal precision. The % RSD on $^{204}$Pb/$^{206}$Pb is however a factor 1.5 better for the drift corrected ratios obtained for $10^{12}$ Ω - $10^{11}$ Ω amplifiers compared to the ratios obtained for the $10^{11}$ Ω - $10^{11}$ Ω amplifier configuration (Fig. 3c and d).
In figure 4, 204Pb/206Pb ratios are plotted against 208Pb/206Pb ratios and compared to the Exponential Mass Fractionation Law (EMFL). For these diagrams, the isotope ratios contained within the dashed lines (Fig. 3) of the five injections are plotted together.

For 10 ppb Pb SRM981, the raw data for both 10^12 Ω - 10^11 Ω and 10^11 Ω - 10^11 Ω amplifier configurations show random variations around the EMFL due to low 204Pb signal (Fig. 4a and b, grey points). In contrast, for 50 ppb Pb SRM981 the raw data of the 10^12 Ω - 10^11 Ω amplifier configuration follow a vertical straight line relative to the x-axis, crossing the EMFL (Fig. 4c, grey points).

According to the model for the evolution of signal ratios during transient signals in a three isotope plot, developed in a recent work 9, this isotope ratio distribution clearly points out that τ^{208}Pb = τ^{206}Pb ≠ τ^{204}Pb. Similarly, from figure 4d, it can be concluded that τ^{208}Pb = τ^{206}Pb = τ^{204}Pb. These observations are consistent with the time constants of the amplifiers which are involved in both configurations for lead multi-collection. After 204Pb/206Pb drift correction (for the 10^12 Ω - 10^11 Ω amplifier configuration) isotope ratios are in better agreement with the EMFL (Fig. 4a and c, black points).

3.3 Internal uncertainty, repeatability and trueness

The isotope ratio uncertainty, trueness and repeatability of the base-line and mass fractionation corrected 204Pb/206Pb ratios for both amplifier configurations, 10^12 Ω - 10^11 Ω and 10^11 Ω - 10^11 Ω, were investigated. The instrumental mass fractionation was corrected internally using the 208Pb/206Pb ratio of SRM981 27 and the exponential mass fractionation law 28, 29.

The weighted mean and the weighted Standard Deviation (SD_w) of the 204Pb/206Pb ratios were calculated for each independent injection using the following equations:

\[ \overline{R}_w = \sum_{i=1}^{n} w_i R_i \] (3)
\[ SD_w = \sqrt{\sum_{i=1}^{n} w_i \left( R_i - \bar{R}_w \right)^2} \] (4)

where, \( w_i \) are the normalized weights calculated on the basis of the point by point \(^{208}\)Pb signals, \( \bar{R}_w \) and \( R_i \) the weighted \(^{204}\)Pb/\(^{206}\)Pb ratio mean and the point by point base line and mass fractionation corrected \(^{204}\)Pb/\(^{206}\)Pb ratios, respectively. For all calculations, only isotope ratios contained within dashed lines (Fig. 3) were considered. In table 3, the \(^{204}\)Pb/\(^{206}\)Pb ratio uncertainty is expressed through the weighted Standard Deviation while the repeatability is the % RSD of the five injections. Trueness is expressed as the difference between the average ratio for the five injections and the reference \(^{204}\)Pb/\(^{206}\)Pb value\(^{27}\).

The results clearly show that in order to benefit from the full performance range of the Faraday multi-collectors when involving \(10^{12} \Omega\) and \(10^{11} \Omega\) amplifiers, isotope signal synchronization for drift correction is important (Table 3).

For 10 ppb SRM981 the drift corrected data point out that the \(10^{12} \Omega - 10^{11} \Omega\) configuration provides 2.6 and 1.7 times lower \(^{204}\)Pb/\(^{206}\)Pb ratio uncertainties and repeatability, respectively, compared to the results provided from the \(10^{11} \Omega - 10^{11} \Omega\) configuration (Fig. 5, table 3). For higher \(^{204}\)Pb signals (50 ppb SRM981) uncertainties obtained by both \(10^{12} \Omega - 10^{11} \Omega\) (drift corrected data) and \(10^{11} \Omega - 10^{11} \Omega\) amplifier configurations are quasi similar. In contrast, repeatability was improved by a factor four when using \(10^{12} \Omega - 10^{11} \Omega\) amplifiers.

Moreover, drift corrected ratios of the \(10^{12} \Omega - 10^{11} \Omega\) configuration showed better performances in terms of ratio trueness compared to the \(10^{11} \Omega - 10^{11} \Omega\) configuration for both 10 ppb and 50 ppb SRM981.

At this point we are interested to assess whether the slight \(^{204}\)Pb/\(^{206}\)Pb ratio trueness bias observed when using the \(10^{12} \Omega - 10^{11} \Omega\) configuration is related to the non-uniform signal attenuation. When \(10^{12} \Omega - 10^{11} \Omega\) amplifiers are involved in multicollection, the theoretical ratio of attenuated signals for peak widths of about 50 s is \(~0.99972\) (Fig.2) which generates a
trueness bias of about –0.028 %. Trueness of the drift corrected $^{204}$Pb/$^{206}$Pb ratios for 50 ppb SRM981 may be explained by this non-uniform signal attenuation (Table 3). In order to test this hypothesis, continuous signal analysis was performed and similar $^{204}$Pb/$^{206}$Pb ratio trueness bias was observed. Moreover, trueness ratio biases were observed for the $10^{11}$ Ω - $10^{11}$ Ω amplifiers which have similar time responses (Table 3). Therefore, we believe that this slight trueness biases are not related to the non-uniform signal attenuation. However, trueness variations are much smaller than the corrected isotope ratio uncertainty, and are therefore not significant.

4 Conclusion

In this work, we considered the simultaneous use of $10^{12}$ Ω and $10^{11}$ Ω amplifiers in multicollection for isotope transient signal detection. We demonstrated that $10^{12}$ Ω amplifiers can be used for transient signal acquisition despite their slow time response compared to the $10^{11}$ Ω amplifiers. We evaluated how the signal attenuation in $10^{12}$ Ω and $10^{11}$ Ω amplifiers is related to the transient signal width. We quantified the bias for the isotopic ratio resulting from the non-uniformly attenuated output signals. This isotopic bias cannot be corrected with the method of internal signal synchronization\(^9\). However, this method is effective for transient signal with durations longer than 30 s, providing accuracies better than 0.1 % for the drift corrected ratios.

This approach has been applied in lead transient signals of a width of ~50 s. As expected, the large time lag between $10^{12}$ Ω and $10^{11}$ Ω amplifiers generated an important isotopic drift which was successfully corrected using the method of internal signal synchronization\(^9\). The drift corrected data showed that for low intensity transient signals (<$10^{13}$ A), the use of $10^{12}$ Ω - $10^{11}$ Ω amplifiers is more beneficial in terms of isotope ratio uncertainty, repeatability and trueness, compared to the $10^{11}$ Ω - $10^{11}$ Ω amplifier configuration. For higher signals (~ 3x$10^{13}$ A), isotope ratio uncertainties obtained by both configurations are similar while repeatability and trueness continue to be better for $10^{12}$ Ω - $10^{11}$ Ω configuration. It would be interesting in a future work, to examine the non-uniform signal attenuation in a $10^{13}$ Ω - $10^{12}$ Ω - $10^{11}$ Ω amplifier configuration\(^{30}\) for isotope transient signals with distinct durations.
Finally, we believe that the use of $10^{12}$ Ω amplifiers for transient signal acquisition opens up new possibilities for the on-line isotope analysis techniques of small sample sizes.

It should be noted that as the method of peak area integration eliminates the artifacts due to the time shift between two transient signals (isotope signals not in phase), it is relevant for transient signal measurements. In addition, this method is effective regardless of the transient signal duration.

For transient signals with duration higher than 30 s and when both $10^{12}$ Ω and $10^{11}$ Ω amplifiers are used, the method of peak integration and the method of signal synchronization applied in this work provide similar isotope ratio trueness and repeatability.

However, the ease of implementation differs for the two methods.

For the peak area integration method, the area to be integrated is a function of the desired measured isotope accuracy. For example, for an accuracy of 0.1%, more than 99.9% of the peak area has to be integrated.

In the case where both $10^{12}$ Ω and $10^{11}$ Ω amplifiers are used, for 99.9% of peak area integration the integrated peak areas of the isotope signals are not defined by the same time intervals (beginning and end of peak integration) due to the important time shift between the isotope signals. The method of peak area integration thus becomes tricky when measurement accuracy better than 0.1% is required and necessitates a detailed analysis of the signal profile in the near-baseline areas where the signal to noise ratio is quite low.

On the contrary, the method of signal synchronization does not depend on the integrated peak area, and can thus be applied to time intervals easily identified by a high signal to noise ratio (e.g. 70% - 90% of the isotopic signal), regardless of the near-baseline peak areas.
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References


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Graphical abstract

This work is a first attempt to evaluate the potential use of $10^{12}$ Ω amplifiers for transient signal isotope analysis and we show for the first time how the transient signal duration influences the accuracy of the isotope ratio measurements.

**MC-ICPMS conditions**

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<td>tandem Cyclone-Scott (SIS)</td>
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<td>Cones</td>
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**MC-ICPMS conditions**

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<td>Sensitivity on $^{208}$Pb (V ppm$^{-1}$, continuous introduction mode)</td>
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**Table 1.** MC-ICPMS operating conditions
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<tr>
<th>Cup configuration</th>
<th>L3</th>
<th>L1</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplifiers</td>
<td>$10^{11}$</td>
<td>$10^{12}$</td>
<td>$10^{11}$</td>
<td>$10^{11}$</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>Isotopes</td>
<td>$^{202}$Hg</td>
<td>$^{204}$Pb</td>
<td>$^{206}$Pb</td>
<td>$^{207}$Pb</td>
<td>$^{208}$Pb</td>
</tr>
</tbody>
</table>

Table 2. Cup and amplifier configuration

<table>
<thead>
<tr>
<th>$^{204}$Pb/$^{206}$Pb</th>
<th>$10^{12}$ - $10^{11}$</th>
<th>$10^{11}$ - $10^{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppb SRM981</td>
<td>Drift uncorrected</td>
<td>Drift corrected</td>
</tr>
<tr>
<td>Average ratio</td>
<td>0.059113</td>
<td>0.059056</td>
</tr>
<tr>
<td>% Uncertainty</td>
<td>2.19</td>
<td>0.98</td>
</tr>
<tr>
<td>% Repeatability</td>
<td>0.47</td>
<td>0.23</td>
</tr>
<tr>
<td>% Trueness</td>
<td>0.159</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.058965</td>
</tr>
<tr>
<td>50 ppb SRM981</td>
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</tr>
<tr>
<td>Average ratio</td>
<td>0.059089</td>
<td>0.058999</td>
</tr>
<tr>
<td>% Uncertainty</td>
<td>2.33</td>
<td>0.35</td>
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<tr>
<td>% Repeatability</td>
<td>0.084</td>
<td>0.028</td>
</tr>
<tr>
<td>% Trueness</td>
<td>0.118</td>
<td>-0.034</td>
</tr>
</tbody>
</table>

Table 3. 10 ppb and 50 ppb SRM981 average $^{204}$Pb/$^{206}$Pb values for five injections of: isotope ratio, uncertainty, repeatability and trueness for both drift uncorrected and drift corrected isotope ratios. Ratio uncertainty is expressed through the average value of the weighted Standard Deviation for five injections while the repeatability is the % RSD of the five $^{204}$Pb/$^{206}$Pb ratio values. Trueness is expressed as the difference between the average ratio for the five injections and the reference $^{204}$Pb/$^{206}$Pb value. Uncertainty and repeatability are expressed for a coverage factor $k = 2$. The reference $^{204}$Pb/$^{206}$Pb value was re-evaluated by Doucelance and Manhès \(^{26}\) and is equal to 0.059019(5).
Figure 1. Schematic circuit diagram of Faraday cup detection system. Where $C$, $R$ and $I$ are the dumping capacity, the high ohmic feedback resistor and the input ion current, respectively. From the Kirchhoff's current law we obtain $I = I_1 + I_2$. Where $I_1$ and $I_2$ are the currents flowing into the capacitor and resistor, respectively.
Figure 2. Percentage of output signal attenuation (solid lines) and ratio of attenuated signals (dashed lines) as a function of transient peak width. The ratio of attenuated signals was calculated by dividing directly: 1) the $10^{12} \Omega$ to $10^{11} \Omega$ output signal attenuations considering a time lag of 0.2 s and 2) the $10^{11} \Omega$ to $10^{11} \Omega$ output signal attenuations considering a time lag of 0.006 s. Shaded area corresponds to the peak widths of this work (~50 s). Horizontal dashed line represents the 0.999 value for the ratio of attenuated signals.
Figure 3. Lead transient signals using a flow injection system directly coupled to the Neptune Plus. For $^{204}\text{Pb}/^{206}\text{Pb}$ ratio acquisition, $10^{12} \Omega - 10^{11} \Omega$ amplifier configuration (on the left side, a and c) and $10^{11} \Omega - 10^{11} \Omega$ amplifier configuration (on the right side, b and d), were respectively used. Grey and black points correspond to raw and drift corrected data, respectively. No isotopic drift was observed for the $10^{11} \Omega - 10^{11} \Omega$ amplifier configuration due to similar amplifier time constants. For all calculations (isotope ratio value, RSD, uncertainty, repeatability, trueness) the zone within the dashed lines was considered.
Figure 4. Three isotope plots for lead transient signals with a flow injection system directly coupled to the Neptune Plus. For $^{204}\text{Pb}/^{206}\text{Pb}$ ratio acquisition, $10^{12}\,\Omega - 10^{11}\,\Omega$ amplifier configuration (on the left side, a and c) and $10^{11}\,\Omega - 10^{11}\,\Omega$ amplifier configuration (on the right side, b and d), were respectively used. For $^{208}\text{Pb}/^{206}\text{Pb}$ ratio acquisition, $10^{11}\,\Omega - 10^{11}\,\Omega$ amplifier configuration was used. Grey and black points correspond to raw and drift corrected data, respectively and the straight line to the Exponential Mass Fractionation Law (EMFL).
Figure 5. Flow injection - MC-ICPMS base line-corrected and mass fractionation-corrected $^{204}\text{Pb}/^{206}\text{Pb}$ ratios for 10 ppb SRM981 (a) and 50 ppb SRM981 (b). Dashed lines represent reference value of $^{204}\text{Pb}/^{206}\text{Pb}$ isotope ratio for the SRM981 standard solution and the shaded areas correspond to the reference value uncertainty (2σ). All isotope ratio uncertainties are expressed for a coverage factor k=2.