International Journal of Mass Spectrometry 300 (2011) 21–25

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Consequences of and potential reasons for inadequate dead time measurements in isotope ratio mass spectrometry

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ARTICLE INFO

Article history:
Received 23 September 2010
Received in revised form
15 November 2010
Accepted 23 November 2010
Available online 2 December 2010

Keywords:
Dead time
Electron multiplier
Isotope ratio measurement
Afterpulsing
Extending/non-extending

ABSTRACT

Precise and accurate determination of the dead time of a pulse counting system is critical for correct isotope ratio determinations. In this paper, potential problems in the determination of dead time are investigated as well as the consequences of using an erroneous value when correcting for dead time. It is shown how the voltage setting of a SEM can affect the dead time of the system. This can be due to an increased pulse height distribution giving after-pulsing effects, which are not corrected for by a detector dead time model. This hypothesis is supported by pulse height measurements of the output signal of the SEM. Output signals of the amplifier and SEM of an Element2 are also studied and the different nature of these signals (extending vs non-extending) and the consequences of this in the correction of dead time count losses are discussed. It is also found that the dead time values determined via isotope ratio measurements can differ with up to 2.7 ns under optimised instrumental settings, and it is also shown that a relatively small difference (2 ns) in the actual dead time of the system and the value used to correct for dead time results in apparent non-linearity of the system which has been reported by other authors.

1. Introduction

In all pulse counting systems a minimum amount of time is required between two pulses for them to be recorded as two separate pulses. The time from the beginning of an incoming pulse till the time when a new pulse can be registered is called the dead time (τ). The linearity of a pulse counting system at high count rates is dependent on a proper correction for dead time. Precise and accurate measurement of the dead time is hence critical for accurate isotope ratio determinations. The overall, or apparent, dead time of a pulse counting system is composed of different dead time components such as the dead times of the secondary electron multiplier and pulse amplifier, as well as possible secondary effects such as afterpulsing. The dead time of a pulse counting system can be characterised both via isotope ratio and electronic measurements. In determination of τ via isotope ratio measurements, the response of the system over the entire counting range of the SEM is measured and an appropriate value of τ is determined [1]. In electronic measurements, the output of an individual electronic component such as the amplifier is characterised either by oscilloscope or by using input from a pulse generator providing double pulses with a variable delay [2,3]. Isotope ratio measurements yield a value of an overall dead time of the whole system including secondary effects, while electronic measurements provide an often more precise determination of τ but only for the individual component that is measured.

A dead time can also be built into an electronic circuit, and one reason to do this is that if the added dead time is large enough it will dominate the dead time of the whole system [3]. This is advantageous since the implemented dead time can be relatively well known and stable. In a previous study, the dead time of the pulse counting system of an Element2 was examined using different settings of an introduced dead time on the pulse amplifier [4]. Both electronic measurements of τ of the pulse amplifier and determinations of τ via isotope ratio measurements were made, and correspondence between electronic and ratio determined dead times was found only for the largest setting of the introduced dead time (70 ns) which suggests that other components than the amplifier affects the apparent dead time of the system. It has also been found that voltage setting and cable impedance can affect the determination of τ due to afterpulsing [5].

Another aspect and possible source of uncertainty in the determination of τ using isotope ratio measurements is introduced from the need to correct for instrumental induced mass bias. Several different models have been proposed for the evaluation of τ from ratio measurements [1,5–7]. The use of a near unity isotope ratio for mass bias correction is naturally favourable, and should enhance the accuracy in determination of τ.

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doi:10.1016/j.ijms.2010.11.018

Table 1
Calculated examples of relative differences in recorded count rates for a non-extending and extending dead time model.

True interaction rate (cps)	Relative difference (%)	
	τ = 16 ns	τ = 50 ns
1.0.E+06	0.01	0.12
2.0.E+06	0.05	0.43
3.0.E+06	0.11	0.89
4.0.E+06	0.18	1.46
5.0.E+06	0.28	2.12

In the literature concerning isotope ratio determinations using MC-ICPMS, several studies have reported non-linearity in measurements involving detection via ion counting [2,8,9]. However, no final explanation for this non-linearity has been provided. This phenomena has been reported to occur when the intensities of the major isotope is above some 50 kcps, and could thus be the result of a difference between the measured τ (used for correcting results) and the actual dead time of the pulse counting system, although the SEM itself may also introduce non-linear effects. The aim of this study is to investigate the effects of using an inadequate measured τ in isotope ratio determinations, and to further study potential problems in the determination of τ.

2. Materials and methods

2.1. Instrumentation

All TIMS measurements were done using an instrument of NBS-type (National Bureau of Standards) [W.R. Shields, National Bureau of Standards (USA), Technical Note No. 426, 1967]. The pulse counting system of this TIMS instrument consisted of a secondary electron multiplier (SEM, MC-Z-19-TRITON, MasCom, Germany), a pulse amplifier (Finnigan MAT262 pulse amplifier, 191290, Finnigan, Germany) and a counter (Hewlett Packard Mod. 53131 A, HP, USA). The pulse amplifier consisted of an internal dead time circuit offering the possibility of changing the electronic dead time of the amplifier. Automatic amplitude distribution measurements of the output pulses from the SEM were performed with a computer controlled (HP Basic) oscilloscope (Infinium Mod. 54845 A, HP, USA). The amplitude was measured for 10,000 wave forms in each pulse height distribution measurement.

All ICP-SFMS measurements were performed using an Element2 (Thermo-Finnigan, Bremen, Germany). The instrument was equipped with a semi-demountable quartz Fassel torch and a CD-2 Guard Electrode. Sample introduction was performed using a concentric nebulizer ("Conikal", GlassExpansion, Melbourne, Australia) and a cyclonic spray chamber ("Twister", GlassExpansion). Self-aspiration, resulting in a sample uptake rate of approximately 0.2 ml min^{-1}, was used throughout the investigation. The guard electrode was grounded and the software induced dead time correction inactivated. Torch position, lens parameters and the nebulizer gas flow rate were optimised daily to obtain maximum sensitivity for $^{238}U^{+}$. All measurements were performed using low resolution ($m/\Delta m$ = 300) with the instrument and data acquisition settings shown in Table 1. The instrument is equipped with an SEM system labelled Multiplier Model MC-SEV-ICP ElementII (MasCom, Bremen, Germany).

Measurements of the output pulses of the SEM were made using a Gage CompuScope 82G (Gage Applied Technologies Inc., Lachine, Canada), plugged in to the J2801 contact of the pulse amplifier board. A solution containing natural uranium of about 1 μg l^{-1} was used, and the magnet mass was set constant to m/z = 238. Waveforms were sampled for about 2 h at a scope sampling rate of 2 GHz. The minimum pulse-to-pulse time then represents the dead time, i.e., the time between the beginning of the trigger pulse and the beginning of the next nearest visible pulse on the scope. The CompuScope was also used to measure pulses directly from the electron multiplier. It was then connected to the BNC contact from the electron multiplier located on the housing of the electrostatic analyzer (ESA).

2.2. Reference materials

The TIMS measurements were performed on IRMM072/6 and the ICP-SFMS measurements on IRMM073/7. Both these standards consist of uranium isotopes where the ratio of $^{235}U/^{238}U$ is approximately 1, and the ratio of $^{233}U/^{238}U$ varies for different subfractions, being 0.019 857(60) for IRMM073/7 and 0.049476(15) for IRMM072/6 (uncertainties are given in parentheses including a coverage factor k = 2 and that apply to the last digits of the given value).

2.3. Evaluation of τ from ratio measurements

From the measurements made on the TIMS instrument, τ was evaluated using the relationship

$$\frac{1}{K_{233/238} \cdot r_{233/238}} = \frac{1}{R_{233/238}} + \tau \cdot I_{238} \cdot \left(\frac{1}{K_{233/238}} - \frac{1}{R_{233/238}} \right) \quad (1)$$

where $R_{233/238}$ is the certified ratio of $n(^{233}U)/n(^{238}U)$, $r_{233/238}$ is the corresponding measured (uncorrected) ratio, $K_{233/238}$ is the corresponding mass-bias correction factor (equals R/r) and I_{238} is the uncorrected intensity of ^{238}U [5]. For determination of τ via isotope ratio measurements on ICP-MS, the relationship suggested by Appelblad and Baxter [7] was applied:

$$r_{238/233} = \frac{I_{238}}{I_{233}} = \frac{R_{238/233}}{K_{238/233}} + \tau \cdot \left(1 - \frac{R_{238/233}}{K_{238/233}} \right) \cdot I_{238} \quad (2)$$

The use of Eq. (1) requires measurements of K separately, while both K and τ can be evaluated from Eq. (2). Hence Eq. (1) is more suited for TIMS measurements where a systematic drift in mass fractionation over the acquisition time can be observed [10], while Eq. (2) requires a non-systematic variation in mass bias and is hence more applicable in ICP-MS measurements. Furthermore, Eq. (2) can be applied in cases were an isotope ratio near unity is not available.

All uncertainties reported in this paper were evaluated in accordance with ISO GUM [11] using the software GUM Workbench [12].

3. Results and discussion

3.1. Afterpulsing

The linearity of a secondary electron multiplier has previously been reported to be dependent on the voltage of the SEM [5,8]. This was further investigated by determination of τ via isotope ratio measurements at different voltage settings of the SEM of an Element2 and a NBS TIMS, and the results are displayed in Fig. 1.

In Fig. 1a, τ determined via isotope ratio measurements at different voltage setting on the SEM of a NBS TIMS instrument is shown. In these measurements, there is a strong trend of decreasing τ with increased voltage of the SEM after a certain threshold voltage. The reason for this effect can be assigned to afterpulsing in the counting system [5]. The possible explanation to afterpulsing is that impedance mismatch will cause signal reflections. High amplitude signals may then return to the amplifier input with amplitude high enough to pass the discriminator level. In such cases, two events will be registered in the amplifier originating from one event in the detector [13]. An improved impedance matching of the electronic system solved this problem.

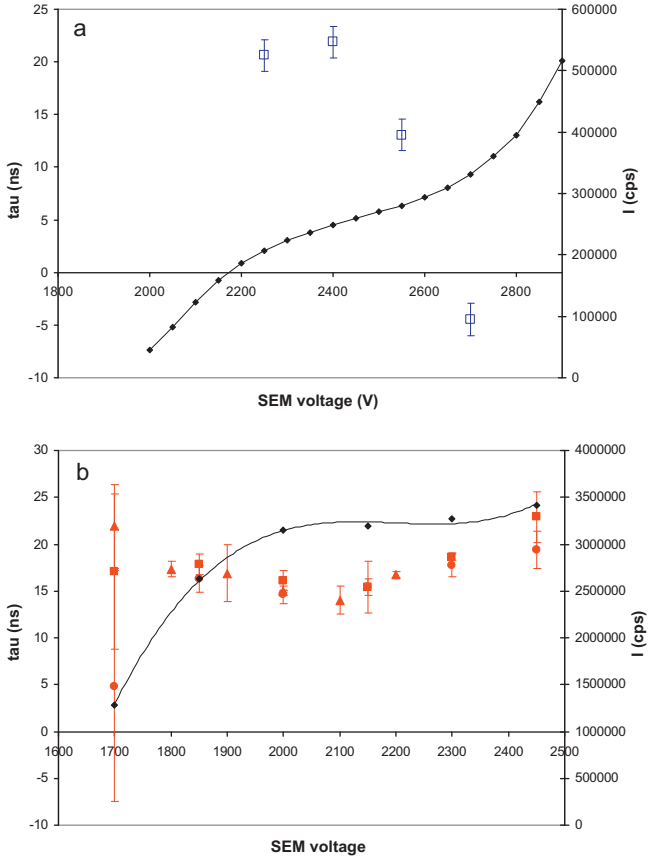

Fig. 1. Relationship between τ (determined via isotope ratio measurements) and SEM voltage. Results from measurements made on the NBS TIMS are shown in (a). Determined values of τ are represented by open squares, and the plateau is represented by filled diamonds. In (b), results from measurements made on the Element2 are shown. Determinations of τ were made with the same instrumental settings on three different occasions, about 2 weeks apart (red triangles, squares and circles). The SEM plateau is displayed as black diamonds. The uncertainty bars represent U ($k=2$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The pulse amplitude distributions at different SEM voltages on the NBS TIMS are shown in Fig. 2. The figure shows that the fraction of higher pulse amplitudes significantly increases at higher SEM voltages. Hence, it is probable that secondary pulses are registered in the amplifier at higher SEM voltages. In previous work timing measurements were done in order to detect secondary pulses [5]. It was found that pulses correlated to a primary incident on the SEM occurred after about 30 ns in that system. However, in this work secondary pulses could still be observed up to about 100 ns. The timing of such secondary pulses is a function of e.g. the length of the cable between the SEM and the amplifier, i.e. the signal transit time in the cable to reach the amplifier a second time. Hence, afterpulsing can for several reasons affect the apparent dead time of a system. Introducing an electronic dead time longer than the timing of the secondary pulses would be one solution to mask such pulses since the detection system would be blind for pulses entering the amplifier input when the system is dead.

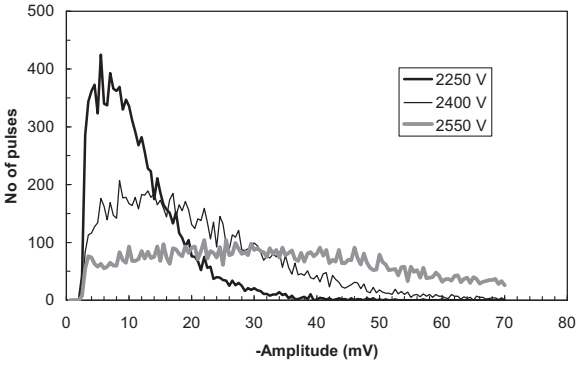

Fig. 2. Pulse height distributions at different SEM voltages. Measurements were made on the NBS TIMS.

In Fig. 1b, the result of a similar study made on an Element2 is shown. It is not possible from these data to state that there is a strong dependency of τ with SEM voltage, but the figure shows a large spread in the results with determined dead times from 15 to 23 ns with a slight tendency towards larger values of τ at larger SEM voltages. The combined standard uncertainties, a few ns, for these measurements are of the same magnitude as those reported by other laboratories [14].

The reason that a strong relationship between determined dead time and SEM voltage was found on one of the instruments but not on the other can be due to differences in the SEM's used, or that the threshold level was not reached in the measurements done on the Element2. However, these results sometimes show a relatively large variation in the determined dead times, even when the SEM voltage is on the plateau. For the Element2, the determined value of τ varies between 14.0 and 16.7 ns for SEM settings between 2100 V and 2200 V, i.e. well on the plateau. The results displayed in Fig. 1a show that adjusting the SEM voltage with only 50 or 100 V on the NBS TIMS may cause a significant change in the behaviour of the system and require updated determination of τ. It was for example observed on the NBS instrument that about three months after the installation of the SEM, the beginning of the plateau moved from about 1800 V to about 2000 V. Hence, frequent adjustment of the SEM voltage is often necessary and care should be taken so that unnecessarily high voltage settings are avoided since this may cause secondary pulses. It should also be kept in mind that recommendation from manufacturers of, e.g., sector field ICPMS, on how to set the SEM voltage allows for quite large variations of the voltage as long as the response is on the plateau. A more standardised procedure should thus be advantageous for precise isotope ratio determinations.

3.2. Dead time of different components

In Fig. 3, the output signals from SEM and amplifier on the Element2 obtained via measurements using an oscilloscope are shown. The pulse width from the SEM is 16 ns, which thus corresponds to the dead time of the SEM. The dead time of the amplifier was set to 70 ns when this measurement was made, and this corresponds with the reading on the oscilloscope. On the amplifier of the Element2, three different settings can be chosen; 10, 20 and 70 ns of which the 10 ns seems to be the default value set by the factory. In a previous study, the different settings were examined and agreement between dead times determined via electronic measurements of the amplifier output and ratio measurements were only obtained when the largest setting, 70 ns, were used [4]. These new measurements showing a pulse width of 16 ns from the SEM provides an explanation to this, i.e., the pulse width of the multiplier being large enough to affect the overall dead time of the system when the introduced dead time of the amplifier is relatively short (10 and 20 ns) [3,13]. In fact, for the lowest setting of 10 ns, the systems showed a dead time that corresponded to the width of the SEM pulse [4].

Hence, the use of electronic measurements in the determination of τ has the potential of providing a precise and accurate value of τ, but it should be kept in mind that this value represents the dead time of that individual component and does not include dead

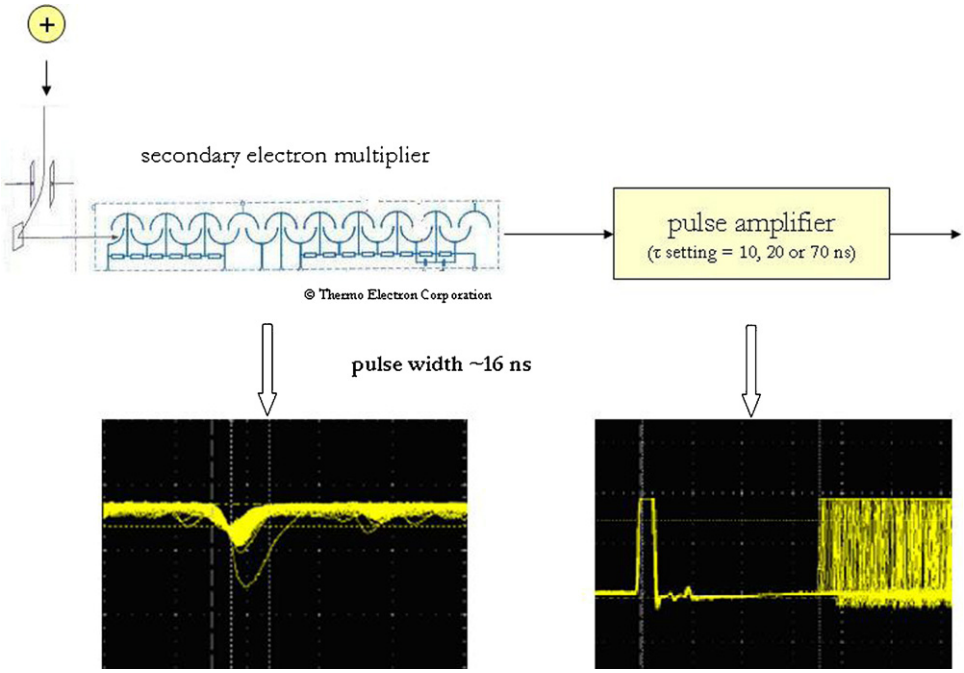

Fig. 3. Output signals from the multiplier and amplifier of the Element2. The dead time of the amplifier was in this measurement set to 70 ns. In the right oscilloscope picture the shortest possible time between the trigger pulse (left square pulse) and the following pulses is ~70 ns. In the left oscilloscope picture it could be found that the width of the SEM-pulse is ~16 ns, representing the dead time of the SEM, which moreover is of the extending type.

times of other components or other more variable effects such as afterpulsing.

3.3. Extending and non-extending dead times

The pictures in Fig. 3 gives rise to another question concerning the nature of the dead time. In the recorded output from the SEM, it can be seen that one pulse is significantly larger than the rest which is due to pile-up of two simultaneously incoming pulses. Usually, the non-extending relationship is used for correction of dead time in mass spectrometric measurements. A non-extending model is characterised by a fixed dead period following a detector event, and this period is not prolonged if a new interaction occurs during the dead period. On the contrary, in an extending dead time system, the initial dead period is prolonged by a new interaction on the detector, i.e. a "new" dead period is triggered by a detector event and started at the time of the new event [13].

Therefore, the nature of the dead time obtained from the pulse width of the multiplier is more likely to be extending since the pulse width increases with pile-up, see Fig. 3. If the dead time of the amplifier is set to 10 ns (the default value), previous measurements show that the system is dominated by the larger dead time of the multiplier which may be extending. The non-extending model is expressed as:

$$i - I = il\tau \tag{3}$$

where i is the true interaction rate and I is the recorded count rate. The extending model is expressed as:

$$I = ie^{-i\tau} \tag{4}$$

The relative difference in observed intensities calculated using the two models for different input intensities and dead times is shown in Table 1. The difference at 5 Mcps and $\tau = 16$ ns is 0.3% which is about equal to the uncertainty in dead time corrected intensity usually obtained in that counting region on the Element2 used in this study. With increased dead time, the relative difference naturally increases. However, due to the non-extending nature of the dead time of the amplifier, the nature of the dead time of the whole system is neither purely extending nor purely non-extending [3,13], and hence the use of Eq. (3) for dead time correction is not entirely correct. However, if the term $i\ \tau$ is small the differences between the models will be insignificant [15]. And by implementing a large non-extending dead time in the system, e.g., in the amplifier, contributions from other sources will be less significant and it will be easier to perform a proper dead time correction. It is though important to keep in mind which model that is used and that the nature of the dead time of the pulse counting system may not entirely correspond with that model. It should also be noticed that it has been recommended by Stresau and Hunter [16] that the pulse width at the discriminator setting should not exceed the dead time of the amplifier in order to avoid effects that cannot be accounted for by corrections using Eq. (3). Hence the default dead time setting of 10 ns on the amplifier of the Element2 should be increased.

3.4. Consequences of inadequate determination of τ

The results presented in Fig. 1a and b show that changes in SEM voltage and/or electronic components of the detection system may cause secondary effects that make a previously determined value of τ too large. Furthermore, the results presented in our previous study [4] show that the use of an electronically determined value of τ may actually result in correction with a too small value since the dead times of other components are not included. In that study, deviations as large as 4–5 ns were found between the electronic determined dead time of the amplifier and the dead time determined via ratio measurements.

An example of the consequence of correcting with a value of τ that differs from the actual dead time, including secondary effects, is shown in Fig. 4. In the figure, results of measurements of IRMM073/7 on the Element2 are shown. The filled circles in the figure represents data corrected with the proper value of τ, in this case 24.1 ns ($U = 0.48$ ns, $k = 2$). As can be seen from the picture, the system is linear over the measured range (up to 4 Mcps). The open

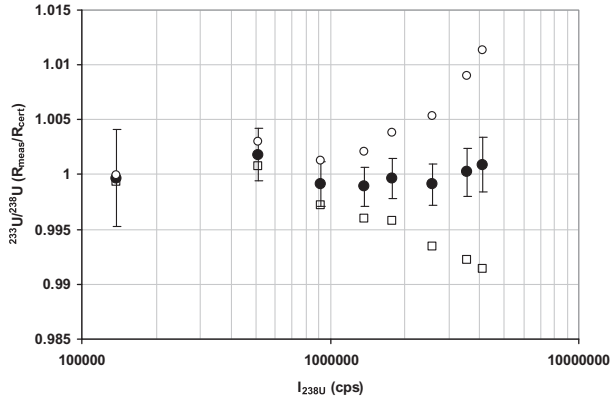

Fig. 4. The effect of correcting with a too high or too low τ. Measurements of IRMM073/7 made on an Element2 with the dead time on the amplifier set to 20 ns. Filled circles represents correction with the proper dead time, $\tau = 24.1$ ns ($U = 0.48$ ns ($k = 2$)). Open squares represents the same data corrected with $\tau = 21.8$ ns and open circles $\tau = 26.2$. The uncertainty bars represent U ($k = 2$).

circles and squares represent the same data corrected with a value of τ that is 2 ns larger or smaller than the correct value of τ. As can be seen from the picture, the deviation from linearity due to the use of these incorrect values of τ is significant and in the order of non-linearity in pulse counting systems reported previously [2,9]. Hence, by altering the value of τ used for dead time correction with only ± 2 ns we achieve an apparent non-linearity in our system and this could implicate that the non-linearity reported by other authors can be a consequence of the difficulty to achieve a properly determined value of τ.

In a recent publication by Richter et al., [14] the standard uncertainty associated with τ determined via isotope ratio measurements varies from 1.3 to 4.6 ns ($k = 2$). The same magnitude of the uncertainty of τ was found in this study as well as in previous measurements performed on the same Element2, where the uncertainty varied from 0.6 to 8.6 ns ($k = 2$) [4]. The major contribution to the uncertainty in dead time measurements using Eq. (2) comes from the uncertainty in the determination of the slope. The uncertainty in τ used for the data in Fig. 4 is 0.48 ns ($k = 2$) which is about the best that has been achieved on our system and comparable with the uncertainty obtained in electronic measurements [4]. If a larger uncertainty of τ is used in the evaluation of R_{meas}/R_{cert}, the uncertainty in the ratio will naturally increase. An uncertainty of, for example, 4 ns ($k = 2$) will result in a relative uncertainty in R_{meas}/R_{cert} of more than 1% for intensities of ^{238}U above 2.5 Mcps, and the non-linearity shown in Fig. 4 will no longer be significant. Hence, when high precision isotope ratio determinations are made using ion counters, an accurate determination of τ including its variation is critical. It is therefore recommended that analysts using ion counters in high precision isotope ratio measurements states not only the magnitude of the dead time including uncertainty, but also the method utilized for the determination of the dead time.

4. Conclusion

The aim of this study was to investigate potential problems in the determination of the dead time of a pulse counting system, and to examine the effects of correcting achieved isotope ratios with an incorrect value of τ. It has been shown that variations in SEM voltage and electronic components of a pulse counting system may alter the apparent dead time of the system, but also that the obtained value of τ from isotope ratio measurements can vary with up to 2.7 ns under optimised SEM conditions. It has also been shown that a relatively small difference (2 ns) between the value of τ used in the correction of measurement results and the actual dead time of the system will cause a significant non-linearity in the system at high count rates. Hence, a continuously updated determination of τ is important in isotope ratio determinations using detection via pulse counting. It is also important that the value of τ is well characterised (truly represents the dead time of the whole system) and that its corresponding uncertainty is incorporated into the uncertainty of the determined isotope ratios in order to avoid erroneous results. The implementation of a large enough, well known dead time in the detection system is advantageous and can mask many of the problems that can be encountered when applying dead time correction.

Following these findings, it can be recommended that first of all a large, well known dead time is set on the amplifier to facilitate dead time correction. The exact magnitude of this dead time, applied late in the signal chain, is somewhat system dependent but a 70 ns dead time of the non-extending type should be sufficient. If that cannot be done, the apparent dead time of the whole system can be affected by several different parameters and correct isotope ratio determinations will need a much more frequent updating of τ.

References

[1] S.M. Nelms, C.R. Quétel, T. Prohaska, J. Vogel, P.D.P. Taylor, J. Anal. Atom. Spectrom. 16 (2001) 333.
[2] D.L. Hoffman, D.A. Richards, T.R. Elliot, P.L. Smart, C.D. Coath, C.J. Hawkesworth, Int. J. Mass Spectrom. 244 (2005) 97–108.
[3] J.W. Müller, Nucl. Instrum. Methods A301 (1991) 543–551.
[4] U. Nygren, H. Ramebäck, M. Berglund, D.C. Baxter, Int. J. Mass Spectrom. 257 (2006) 12–15.
[5] H. Ramebäck, M. Berglund, D. Vendelbo, R. Wellum, P.D.P. Taylor, J. Anal. Atom. Spectrom. 16 (2001) 1271–1274.
[6] A. Held, P.D.P. Taylor, J. Anal. Atom. Spectrom. 14 (1999) 1075–1079.
[7] P.K. Appelblad, D.C. Baxter, J. Anal. Atom. Spectrom. 15 (2000) 557–560.
[8] S. Richer, S.A. Goldberg, P.B. Mason, A.J. Traina, J.B. Schwieters, Int. J. Mass Spectrom. 206 (2001) 105–127.
[9] L. Ball, K.W.W. Sims, J. Schwieters, J. Anal. Atom. Spectrom. 23 (2008) 173–180.
[10] H. Ramebäck, M. Berglund, R. Kessel, R. Wellum, Int. J. Mass Spectrom. 216 (2002) 203–208.
[11] Guide to the Expression of Uncertainty in Measurement, International Organisation for Standardisation, Geneva, Switzerland, 1995.
[12] GUM Workbench, Metrodata GmbH, D-79639 Grenzach-Whylen, Germany, 1999.
[13] G.F. Knoll, Radiation Detection and Measurement, 3rd edn., John Wiley & Sons, NY, USA, 2000, pp. 119–122.
[14] S. Richter, A. Alonso, Y. Aregbe, R. Eykens, F. Kehoe, H. Kühn, N. Kivel, A. Verbruggen, R. Wellum, P.D.P. Taylor, Int. J. Mass Spectrom. 281 (2009) 115–125.
[15] J.M. Hayes, D.A. Schoeller, Anal. Chem. 49 (1997) 306–311.
[16] D. Stresau, K. Hunter, in: S. Nelms (Ed.), Inductively Coupled Plasma Mass Spectrometry Handbook, Blackwell Publishing Ltd., Oxford, UK, 2005 (Chapter 3).