Designation: E2426 – 10

Standard Practice for Pulse Counting System Dead Time Determination by Measuring Isotopic Ratios with SIMS[1]

This standard is issued under the fixed designation E2426; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice provides the Secondary Ion Mass Spectrometry (SIMS) analyst with a method for determining the dead time of the pulse-counting detection systems on the instrument. This practice also allows the analyst to determine whether the apparent dead time is independent of count rate.

1.2 This practice is applicable to most types of mass spectrometers that have pulse-counting detectors.

1.3 This practice does not describe methods for precise or accurate isotopic ratio measurements.

1.4 This practice does not describe methods for the proper operation of pulse counting systems and detectors for mass spectrometry.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)[3]

2.2 *ISO Standards:*[4]

ISO 21270 Surface Chemical Analysis—X-ray photoelectron and Auger electron spectrometers—Linearity of intensity scale; and references 1, 2, 10, 13 and 14 therein.

3. Terminology

3.1 *Definitions:*

3.1.1 See Terminology E673 for definitions of terms used in SIMS.

3.1.2 See Terminology ISO 21270 for definitions of terms related to counting system measurements.

3.1.3 *isotopic ratio, n*—written as $^{m2}X/^{m1}X$, for an element X with isotopes $m1$ and $m2$, refers to the ratios of their atomic abundances. When it is a value measured in a mass spectrometer it refers to the ratio of the signal intensities for the two species.

3.1.3.1 *Discussion*—The notation $\Delta^{m2}X$ or $\delta^{m2}X$ refers to the fractional deviation of the measured isotopic ratio from the standard ratio or reference. In this practice, $\Delta^{m2}X$ will refer to the fractional deviation of the measured ratio, uncorrected for mass-fractionation (see 3.1.4) and $\delta^{m2}X$ will refer to the fractional deviation of the measured ratio that has been corrected for mass-fractionation. An example for magnesium (Mg) is:

$$\Delta^{25}\mathrm{Mg} = \frac{\left(^{25}\mathrm{Mg}/^{24}\mathrm{Mg}\right)_{Meas}}{\left(^{25}\mathrm{Mg}/^{24}\mathrm{Mg}\right)_{Ref}} - 1 \quad (1)$$

where:

$(^{25}\mathrm{Mg}/^{24}\mathrm{Mg})_{Ref} = 0.12663$[5].

3.1.4 *mass-fractionation, n*—sometimes called "mass-bias," refers to the total mass-dependent, intra-isotope variation in ion intensity observed in the measured isotopic ratios for a given element compared with the reference ratios. It can be expressed as the fractional deviation per unit mass.

3.1.4.1 *Discussion*—The mass of an isotope i of element X (^{mi}X) shall be represented by the notation m_i, where "i" is an integer.

4. Summary of Practice

4.1 This practice describes a method whereby the overall effective dead time of a pulse counting system can be determined by measuring isotopic ratios of an element having at least 3 isotopes. One of the isotopes should be approximately

[1] This practice is under the jurisdiction of ASTM Committee E42 on Surface Analysis and is the direct responsibility of Subcommittee E42.06 on SIMS.

Current edition approved June 1, 2010. Published July 2010. Originally approved in 2005. last previous edition approved in 2006 as E2426 – 05 (2006). DOI: 10.1520/E2426-10.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, http://www.iso.ch.

[5] Catanzaro, E. J., Murphy T. J., Garner E. L., and Shields W. R., "Absolute Isotopic Abundance Ratios and Atomic Weight of Magnesium," *Journal of Research of the National Bureau of Standards*, Vol 70a, 1966, pp. 453–458.

a factor of 10 more abundant than the others so that a first order estimate of the dead time can be calculated that will be close to the true value. The efficacy of the method is increased if the sample is flat and uniform, such as a silver (Si) wafer or a polished metal block so that the count rate of the isotopes varies minimally during the individual measurements.

5. Significance and Use

5.1 Electron multipliers are commonly used in pulse-counting mode to detect ions from magnetic sector mass spectrometers. The electronics used to amplify, detect and count pulses from the electron multipliers always have a characteristic time interval after the detection of a pulse, during which no other pulses can be counted. This characteristic time interval is known as the "dead time." The dead time has the effect of reducing the measured count rate compared with the "true" count rate.

5.2 In order to measure count rates accurately over the entire dynamic range of a pulse counting detector, such as an electron multiplier, the dead time of the entire pulse counting system must be well known. Accurate count rate measurement forms the basis of isotopic ratio measurements as well as elemental abundance determinations.

5.3 The procedure described herein has been successfully used to determine the dead time of counting systems on SIMS instruments.[6] The accurate determination of the dead time by this method has been a key component of precision isotopic ratio measurements made by SIMS.

6. Apparatus

6.1 The procedure described here can be applied to any mass spectrometer, including SIMS, with a pulse counting system.

7. Procedure

7.1 Choose a sample of the appropriate material to make the measurements simple and uncomplicated by issues such as charging or geometry. The material should be a conductor, or semiconductor. It should be polished flat and mounted in a suitable manner for analysis in the SIMS instrument. The element to be measured should have at least 3 isotopes with one being approximately 10 times more abundant than the others. The signal obtained from the most abundant isotope will be used as the denominator to form all of the isotopic ratios. Examples of this kind of element are: Si, Mg, and titanium (Ti).

7.1.1 The dead time of a counting system can be characterized as either retriggerable (paralyzable, or extendable), non-retriggerable (non-paralyzable, or non-extendable), or a combination of the two. In a retriggerable system the length of the discriminator output pulse is increased if a pulse arrives at the discriminator input before the output has returned to its quiescent state. Some systems have an additional recovery time after the output has returned to its quiescent state during which they will not react to input pulses. This time just adds to the system dead time. In such a system the dead time is given by:

$$C_{Meas} = C_{True} e^{-\tau C_{True}} \quad (2)$$

where:

C_{Meas} = the measured count rate,
C_{True} = the true count rate, and
τ = the dead time.

7.1.1.1 In a non-retriggerable system a pulse is simply ignored if it arrives before the discriminator output has returned to its quiescent state (plus some recovery time). In such as system the dead time is given by:

$$C_{Meas} = \frac{C_{True}}{1 + C_{True} \times \tau} \quad (3)$$

7.1.1.2 These two equations, for each type of system, yield the same result to first order. Thus, for the purposes of this guide we will assume that Eq 4 adequately describes the system in question:

$$C_{Meas} = C_{True} \times (1 - \tau \times C_{True}) \quad (4)$$

7.1.2 The procedure for computing the dead time from isotopic ratio measurements involves effectively computing two quantities: the dead time, and the mass fractionation. In order to do this, the fractional deviations (see 3.1.1.1) for each of the minor isotopes is computed and then fitted to a line as a function of mass. Fig. 1 shows a representation of a plot for a typical 3-isotope system where, in this case, isotope 1 is used as the reference isotope.

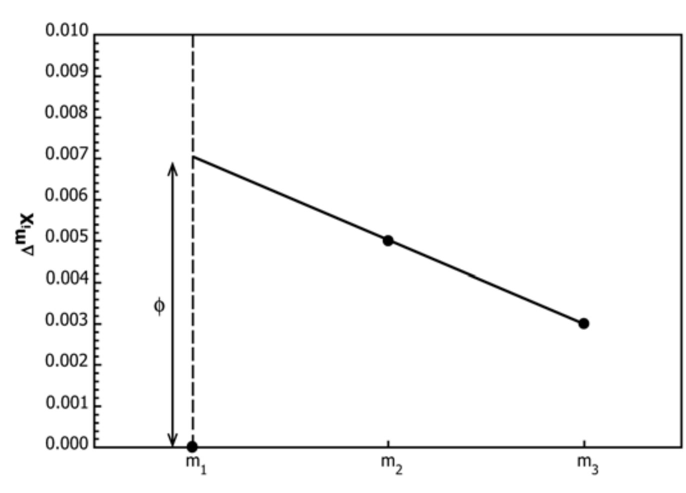

FIG. 1 Representation of the Effects of Dead Time and Mass Fractionation on Measured Isotopic Ratios Expressed as Fractional Deviations

[6] Fahey, A. J., "Measurements of Dead Time and Characterization of Ion Counting Systems for Mass Spectrometry," *Review of Scientific Instruments*, Vol 69, 1998, p. 1282.

7.1.2.1 For this system the distance "φ" shown in the plot is given by:

$$\varphi = \Delta^{m2}X + (m_2 - m_1)\frac{(\Delta^{m2}X - \Delta^{m3}X)}{(m_3 - m_2)} \quad (5)$$

where:

m_1, m_2, and m_3 = the masses of each of the measured isotopes.

7.1.2.2 This equation takes into account mass bias, and computes the magnitude of the dead time effect on the major isotope. The first order estimate of the dead time can be simply computed from:

$$\varphi = {}^{m1}X_{Meas} \times \tau \quad (6)$$

where:

τ = the dead time, given the assumption that ${}^{m1}X_{meas} \approx {}^{m1}X_{True}$.

7.1.2.3 This approximation could be iterated to achieve a more precise estimate of the dead time. In addition, mass fractionation dependencies other than linear could be used.

7.1.3 This procedure can be extended to systems with more than 3 isotopes so that a fit can be performed to the minor isotope ratios, such as with an element like Ti.

7.1.4 Uncertainties can be assigned to the computed dead time through normal propagation of errors. This uncertainty can then be used in the computation of measured isotopic ratios for other elements. The uncertainty in the dead time may be a significant factor in some high-precision isotopic ratio measurements.

7.1.5 The dead time can be measured as a function of the count rate of the major isotope by making isotopic ratio measurements at various count rates of the major isotope. To control the count rates one can vary the width of the mass spectrometer entrance slit or by changing the source intensity in some other way. Ideally one expects the dead time to be independent of count rate. This may not be the case if, for example, the pre-amplifier is AC-coupled to the discriminator and the input voltage to the discriminator changes as a function of count rate. Thus, a measurement of the dead time as a function of count rate can give the analyst an indication of whether the counting system is functioning as expected.

8. Keywords

8.1 dead time; isotopic ratios; pulse counting; SIMS