Correction of dead time effects in laser-induced desorption time-of-flight mass spectrometry: Applications in atom probe tomography

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ABSTRACT

Dead time effects in time-of-flight secondary ion mass spectrometry are well known and can be corrected for using Poisson statistics. Laser-induced desorption, however, introduces nonlinearity in the evaporation process resulting in highly fluctuating signals that make proper dead time correction much more challenging. Here, we propose a modified dead time correction procedure that overcomes such obstacles using data from correlated detection events from different isotopes of a single element. Provided the signals are not affected by unresolved mass interferences, this dead time correction enables us to obtain meaningful isotope ratios as demonstrated for atom probe tomography data of carbon from nanodiamonds and of silicon.

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1. Introduction

Any detector is able to reliably distinguish between different events only if they are separated from each other sufficiently either in time or in space. The duration a detector needs to recover after a counting event in order to be able to detect a second event following shortly afterwards is described as the dead time of the detector. It should be clarified that detector in this context describes the entire detection system typically consisting of several components such as the actual detector, typically a photomultiplier or microchannel plate, a discriminator that accepts signals as counting events or rejects them as electronic noise, and a time digitizer, which converts time intervals into digital representations.

In favorable cases, statistical approaches can be used to correct for dead time effects in order to calculate the signal intensities that an ideal detector with no dead time would have delivered. Dead time correction in time-of-flight mass spectrometry (TOF-MS) is complicated by the fact that signal intensities vary on very short time scales. However, such highly fluctuating signals can often be corrected for dead time effects as described in the literature [1]. Correction is possible since each measurement usually averages over a large number of ionization events that, except for statistical fluctuations, are uniform in ionization yield. This is typically fulfilled, e.g., in time-of-flight secondary ion mass spectrometry (TOF-SIMS) as long as the measurement is restricted to a homogeneous sample or sample region and neither sample properties nor primary ion beam intensity vary significantly during the analysis. Here, dead time correction works well and is now standard protocol during quantitative data evaluation [2–4]. An interlaboratory study involving 21 TOF-SIMS instruments has shown that this dead time correction is generally applicable and robust [5].

However, for some TOF-MS techniques, ionization yield is not constant and the dead time correction described by Stephan et al. [1] could not be applied. This is especially the case in techniques where laser-induced desorption is used, e.g., in laser desorption resonance ionization mass spectrometry (RIMS). As described by Savina et al. [6], the desorption process is nonlinear in laser

pulse energy, and moderate fluctuations lead to large variations in the desorbed particle flux. Desorption lasers are therefore often operated in a very low power regime, where particles are desorbed only occasionally, in order to avoid relatively powerful laser pulses that would release many particles in a single shot [6]. Very low count rates are the consequence, and measurement times have to be increased drastically to achieve sufficient counting statistics, if high precision is required.

This is also the case in atom probe tomography (APT), which combines field evaporation triggered by pulsing from a focused ultraviolet laser in a constant electric field with TOF-MS [7,8]. Using APT in order to measure isotope ratios in nanoparticles would be highly desirable in particular for cosmochemical applications, e.g., to study the origin of meteoritic nanodiamonds [8]. However, such data so far suffer from instrumental biases [8] among which dead time effects seem to play a major role. Therefore, most APT applications until now focused on the elemental composition of samples, where high accuracy is less crucial, as it was previously impossible to get useful isotope ratios.

However, the importance of multi-hit events causing dead time effects, also referred to as pile-up or detector saturation, for interpretation of mass spectra in APT has been recognized in the field. It has been identified already in 1978 that atom probe data do not directly give the true composition of a sample and that Poisson statistics could be applied for correction [9]. In 1984, Cerezo et al. developed a statistical correction without making any prior assumptions as to the distribution of ions per pulse [10]. In 1988, Menand et al. made a similar approach but made use of double counting events [11]. More recently, methods such as a contingency table approach have been employed to study correlations in field evaporation and to improve quantification of measured compositions [12].

Here, we present a dead time correction of APT isotope data using Poisson statistics but avoiding some of the deficiencies from previous studies and apply this correction to carbon and silicon data [8]. By using correlated counting events from isotopes of the same element, the method presented here allows correction of APT data from ion species that vary significantly in their evaporation behavior with some elements being more prone to evaporation in multiples than others.

2. Counting statistics

In the following, we will focus on the simple case, where for one laser pulse, only one ion per species can be detected, and different species are separated by a sufficient time gap so that they do not interfere with each other. From Eq. (8) in Stephan et al. [1],

$$^aE = -N \cdot \ln\left(1 - \frac{a}{N}\right) \quad \text{and} \quad ^bE = -N \cdot \ln\left(1 - \frac{b}{N}\right). \tag{1}$$

Here, ^aE and ^bE describe the corrected peak integrals or *true intensities* for two isotopes of an element E, whereas a and b represent the *measured intensities* for these isotopes, and N is the number of ionization events. It should be clarified here that, in general, the number of ionization events is smaller than the number of pulses from the desorption laser, if we assume that many laser pulses do

not have the potential to cause ionization of the element of interest. This is different from TOF-SIMS, where each primary ion pulse is considered an ionization event, and N is a known quantity. For laser-induced desorption, N is unknown and may depend on the ion species. N is not the number of pulses in which ionization occurs; rather, it can be best described as the number of laser pulses where the conditions for formation of a given ion species are met. However, we can assume that N is identical for different isotopes of the same element and that isotope effects on desorption yields can be neglected.

2.1. The number of ionization events

If we now assume that detection of both isotope species is independent, the probability of detecting a correlated event, where both isotopes are detected in a single ionization event, is

$$\frac{c}{N} = \frac{a}{N} \cdot \frac{b}{N}. \tag{2}$$

Here, c is the number of laser pulses for which both isotopes are detected. N can therefore be calculated as

$$N = \frac{a \cdot b}{c}. \tag{3}$$

For the statistical error ΔN, one has to take into account that a and b are not independent from c. We therefore introduce

$$a' = a - c \quad \text{and} \quad b' = b - c \tag{4}$$

as independent variables, since they are the number of counting events for both isotopes not including the number of correlated events given by c. Eq. (3) now becomes

$$N = \frac{(a' + c)(b' + c)}{c}. \tag{5}$$

The statistical error ΔN now follows from the error propagation theorem as

$$\Delta N = \sqrt{\left(\frac{b' + c}{c}\Delta a'\right)^2 + \left(\frac{a' + c}{c}\Delta b'\right)^2 + \left(\left(1 - \frac{a' \cdot b'}{c^2}\right)\Delta c\right)^2}. \tag{6}$$

Using the original variables a and b, this can also be written as

$$\Delta N = \sqrt{\left(\frac{b}{c}\Delta a'\right)^2 + \left(\frac{a}{c}\Delta b'\right)^2 + \left(\frac{a + b - N}{c}\Delta c\right)^2}. \tag{7}$$

2.2. Peak integrals

Using Eq. (3), the peak integral ^aE from Eq. (1) can be calculated as

$$^aE = -\frac{a \cdot b}{c} \cdot \ln\left(1 - \frac{c}{b}\right). \tag{8}$$

For calculation of the statistical errors, independent variables are needed

$$^aE = -\frac{(a' + c)(b' + c)}{c} \cdot \ln\left(\frac{b'}{b' + c}\right). \tag{9}$$

Then, the statistical error becomes

$$\Delta^aE = \sqrt{\left[\left(\frac{b' + c}{c} \cdot \ln\left(\frac{b'}{b' + c}\right)\right)\Delta a'\right]^2 + \left[\left(\frac{a' + c}{b'} + \frac{a' + c}{c}\ln\left(\frac{b'}{b' + c}\right)\right)\Delta b'\right]^2 + \left[\left(\frac{a' + c}{c} + \left(\frac{a' \cdot b'}{c^2} - 1\right)\ln\left(\frac{b'}{b' + c}\right)\right)\Delta c\right]^2}. \tag{10}$$

Using the original variables a and b, this can also be written as

$$\Delta^aE = \sqrt{\left[\left(\frac{b}{c} \cdot \ln\left(1 - \frac{c}{b}\right)\right)\Delta a'\right]^2 + \left[\left(\frac{a}{b - c} + \frac{a}{c}\ln\left(1 - \frac{c}{b}\right)\right)\Delta b'\right]^2 + \left[\left(\frac{a}{c} + \left(\frac{a \cdot b}{c^2} - \frac{a + b}{c}\right)\ln\left(1 - \frac{c}{b}\right)\right)\Delta c\right]^2}, \tag{11}$$