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A drift correction optimization technique for the reduction of the inter-measurement dispersion of isotope ratios measured using a multi-collector plasma mass spectrometer

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ABSTRACT

The effects of polynomial interpolation and internal standardization drift corrections on the inter-measurement dispersion (statistical) of isotope ratios measured with a multi-collector plasma mass spectrometer were investigated using the (analyte, internal standard) isotope systems of (Ni, Cu), (Cu, Ni), (Zn, Cu), (Zn, Ga), (Sm, Eu), (Hf, Re) and (Pb, Tl). The performance of five different correction factors was compared using a (statistical) range based merit function ω_m which measures the accuracy and inter-measurement range of the instrument calibration. The frequency distribution of optimal correction factors over two hundred data sets uniformly favored three particular correction factors while the remaining two correction factors accounted for a small but still significant contribution to the reduction of the inter-measurement dispersion.

Application of the merit function is demonstrated using the detection of Cu and Ni isotopic fractionation in laboratory and geologic-scale chemical reactor systems. Solvent extraction (diphenylthiocarbazone (Cu, Pb) and dimethylglyoxime (Ni)) was used to either isotopically fractionate the metal during extraction using the method of competition or to isolate the Cu and Ni from the sample (sulfides and associated silicates). In the best case, differences in isotopic composition of ±3 in the fifth significant figure could be routinely and reliably detected for Cu65/63 and Ni61/62.

One of the internal standardization drift correction factors uses a least squares estimator to obtain a linear functional relationship between the measured analyte and internal standard isotope ratios. Graphical analysis demonstrates that the points on these graphs are defined by highly non-linear parametric curves and not two linearly correlated quantities which is the usual interpretation of these graphs. The success of this particular internal standardization correction factor was found in some cases to be due to a fortuitous, scale dependent, parametric curve effect.

1. Introduction

Signal drift is a feature common to all types of analytical plasma spectrometers and is particularly problematic for mass spectrometry because the plasma to mass spectrometer interface exposes sensitive parts of the instrument (ion lenses, sampler and skimmer) to fouling during sample analysis [1,2]. The need to accurately and reliably account for the drift error is particularly acute for stable isotope ratios where inter-measurement variances of $\leq\pm1\times10^{-5}$ may be necessary for some applications [3]. The physical causes of signal drift in plasma spectrometers are rarely identified, monitored or controlled and there are many possible causes [1,2,4]. Diagnostic techniques have been developed [5,6] but usually a mathematical correction is used to account for the determinate error caused by the drift [4,7–13]. A peculiar (and unexplained) feature of signal and signal quotient drift is the wide range of curve shapes reported in both plasma optical emission and plasma mass spectrometry [9,10,13]. The order n of interpolating polynomials ranges up to the sixth power for signal and signal quotient drift curves in plasma spectrometry and changes from day-to-day.

The origins of the complexity of signal and signal quotient drift curves can be readily understood. Let the signal be represented by a multi-dimensional signal response surface $S(\boldsymbol{x}_0, \boldsymbol{x}_1, \ldots, \boldsymbol{x}_p)$ where the $\boldsymbol{x}$'s represent the physical factors (pressure, temperatures, voltages, etc.) which affect the signal strength. Drift is represented by considering the $\boldsymbol{x}$ to be time dependent variables $\boldsymbol{x}(t)$. The $\boldsymbol{x}(t)$ are assumed to be of the form $\boldsymbol{x}(t) = \Sigma a_n t^n$ [7]. Generally there is no physical reason to restrict the value of n for any $\boldsymbol{x}(t)$. When $n > 0$ for one or more of the $\boldsymbol{x}(t)$ then the time-ordered set of $(\boldsymbol{x}_0(t), \boldsymbol{x}_1(t), \ldots, \boldsymbol{x}_p(t))$ points defines a single parametric curve (the hardware drift line) on the coordinate

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axis plane of S. The intersection of the perpendicular projection of the hardware drift line onto the surface S yields a set of time ordered points (t, S(t)) which defines the signal drift curve of a run. If all the $\boldsymbol{x}(t)$ have $n > 0$ then the signal drift curve meanders over the surface. If at least one of the $\boldsymbol{x}(t)$ is constant *k*, (e.g., sampling position in the plasma) then the hardware drift curve is a straight line along which the time ordered set of (k, $\boldsymbol{x}_1(t)$, ..., $\boldsymbol{x}_p(t)$) travel, changing direction and speed along this line according to the parametric hardware drift curve defined in exclusion of any constant $\boldsymbol{x}(t)$ (i.e., the time-ordered set of ($\boldsymbol{x}_1(t)$, ..., $\boldsymbol{x}_p(t)$) points). This is the usual experimental situation in analytical plasma spectrometry.

Parametric curves are well-known for their utility in obtaining exotic curve shapes (Lissajous figures, cycloids etc.) useful in engineering applications. That same property could be a disadvantage for analytical work since the hardware drift line may contain many points where the slope is undefined or zero with corresponding discontinuities in the curve defined by the set of points (t, S(t)). It is known in plasma spectrometry that level curves of the signal with respect to changes in a primary instrument signal response factor (rf power, nebulizer pressure, plasma sampling location) are typically concave downward signal response functions of the $\boldsymbol{x}$ [14–18]. A typical operating point is usually located close to the global maxima where the change in S per unit step along the coordinate axis (in any direction) is relatively small. Also, plasma spectrometers usually have signal drift rates of a fraction of a percent per hour. The combination of a shallow gradient and small drift rate attenuates the effect that the abrupt changes in the slope of the hardware drift line have on the continuity of the curve defined by the set of points (t, S(t)). In this situation signal drift curves are usefully approximated as a polynomial [9,13].

The signal quotient $S_i(t)/S_j(t)$ is a rational function which, in general, cannot be approximated as a polynomial except under well-defined circumstances. Consider the case where $\boldsymbol{x}(t)$ represents the nebulizer gas pressure P. On the multi-collector instrument isotope ion signals of the same element may have a very small offset between the ordinate values of the maxima of two isotope ion signals $S_i(P)$ and $S_j(P)$ but the orders of the polynomials of $S_i(P)$ and $S_j(P)$ are going to be the same and the normalized curvatures of $S_i(P)$ and $S_j(P)$ are identical when i and j are of the same element [18]. Under those conditions the rational function $S_i(P)/S_j(P)$ is well-approximated by a polynomial function of P at operating points in the neighborhood of the level curve maxima [18]. On the assumption that this approximation is true of the other $\boldsymbol{x}(t)$, a polynomial approximation of $S_i(t)/S_j(t)$ is analytically useful. For example, consider the signal response surface defined as $S(\boldsymbol{x}_0(t), \boldsymbol{x}_1(t)) = \exp(-((\boldsymbol{x}_0(t))^2 + (\boldsymbol{x}_1(t))^2 - k\,\boldsymbol{x}_0(t)\boldsymbol{x}_1(t))$ where k is a real constant > 0, $\boldsymbol{x}_0(t)$ and $\boldsymbol{x}_1(t)$ are linear and quadratic functions respectively. S is a simplified form of the bivariate Gaussian function which has approximately the correct shape. Over restricted ranges of t the isotope ratio curves, $IR(t) = S_i(t)/S_j(t)$, are very well-approximated ($r^2 = 1.0$) by polynomials (Fig. 1). Small changes in the coefficients of S and the $\boldsymbol{x}(t)$ resulted in the polynomial order of $S_i(t)/S_j(t)$ ranging from the first to the sixth order. This is a typical range for signal ratios at run times of several hours [9].

There is also the difficulty of the stability of the rational function $S_i(t)/S_j(t)$. Small errors in the values of the coefficients of $S_i(P)$ and $S_j(P)$ can result in large errors in the calculated quotient [18] and this is referred to as the rational function effect. This effect would be potentially troublesome for signals which are drifting according to $\Sigma a_n t^n$ even if the correction calculations use the raw isotope ratios rather than correcting the signals themselves; the underlying rational function effect is still present in the ratio data.

1.1. Ratio drift correction factors

In general, the simplest choice among possible drift correction factors is between interpolating polynomials and internal standardization.

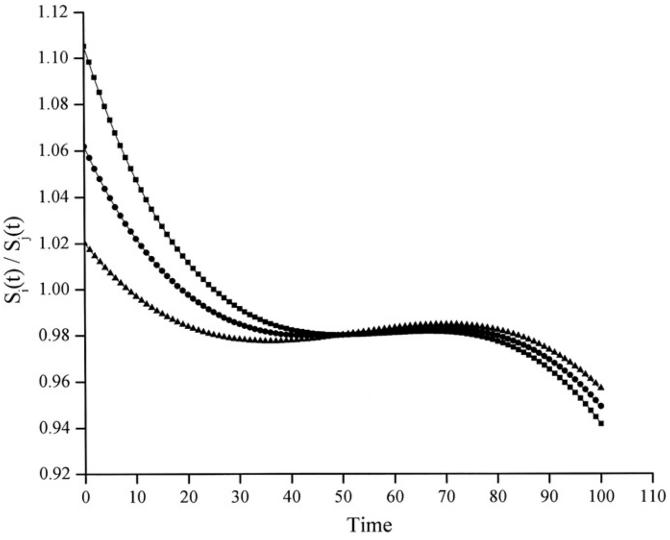

Fig. 1. Calculated values of $S_i(t)/S_j(t)$ where $S_i(t)$ and $S_j(t)$ are calculated as $S(\boldsymbol{x}_0(t), \boldsymbol{x}_1(t)) = \exp(-((\boldsymbol{x}_0(t))^2 + (\boldsymbol{x}_1(t))^2 - k\boldsymbol{x}_0(t)\boldsymbol{x}_1(t))$ and $\boldsymbol{x}_0(t) = a_1 t + 1$, $\boldsymbol{x}_1(t) = t^2 + t + 1$. Values of k for S_i and S_j were 0.99 and 0.995 respectively. The least squares polynomial regression lines of (t, IR(t)) found $n = 5$, $r^2 = 1.0$. The values of a_1 for $\boldsymbol{x}_0(t)$ are 1.0 (squares), 0.8 (circles) and 0.6 (triangles).

Define the drift correction factor, R(t), as $R(t) = IR(t)/IR_T$ where IR(t) is the value of an isotope ratio (measured or calculated) at time t and IR_T is the known value. The polynomial drift correction factor is

$$R_A(t) = \left(\sum a_n t^n\right)/((IR_A)_T)_{Std} \tag{1}$$

where the subscript A refers to the analyte, $((IR_A)_T)_{Std}$ is the known value of the analyte ratio in the reference ratio solution. Although this equation is innocuous enough the model selection problem [19–22] becomes an issue for multi-collector isotope ratio measurements. The probability density functions of S and IR are unknown, non-Gaussian distributions [18] and the usual statistical techniques for optimizing the value of n (which were developed for Gaussian variables) are not applicable (see Section 1.2) and possibly not very useful for isotope ratio measurements using a multi-collector instrument (see Section 3.4). Optimization of n is discussed after the merit function ω_m is introduced in Section 3.2.

The internal standardization drift correction factor is, from the definition of R(t),

$$R_A(t) = k(t)(IR_A(t)/IR_{IS}(t))$$

where the subscript IS refers to the internal standard, $k(t) = R_{IS}(t) * ((IR_{IS})_T / (IR_A)_T)_{Std}$, $R_{IS}(t)$ is always known and the quotient of the true ratios in the reference ratio solution is a known constant of the run. There are two possible $R_A(t)$ factors:

i) using the optimized least squares solutions of $IR_A(t)$ and $IR_{IS}(t)$ from Eq. (1), the value of $R_A(t)$ is

$$R_A(t) = k(t)\left(\sum a_n t^n / \sum b_m t^m\right) \tag{2}$$

ii) alternatively

$$R_A(t) = k(t)\sum a_n t^n \tag{3}$$

where the rational function of Eq. (2) is now being represented by a least squares fitted polynomial rather than using the experimentally determined rational function (Eq. (2)).