

A Drift Correction Procedure

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A procedure is introduced that can mitigate the deleterious effect of low-frequency noise—often termed drift—on the precision of an analytical experiment. This procedure offers several performance benefits over traditional designs based on the periodic measurement of standards to diagnose and correct for variation in instrument response. Using repeated measurements of every sample as a drift diagnostic, as opposed to requiring the periodic measurement of any given sample or standard, the analyst can better budget the measurement time to be devoted to each sample, distributing it to optimize the uncertainty of the analytical result. The drift is diagnosed from the repeated measurements, a model of the instrument response drift is constructed, and the data are corrected to a “drift-free” condition. This drift-free condition allows data to be accumulated over long periods of time with little or no loss in precision due to drift. More than 10-fold precision enhancements of analytical atomic emission results have been observed, with no statistically significant effects on the means. The procedure is described, performance data are presented, and matters regarding the procedure are discussed.

Analytical instruments transduce chemical properties to a signal, which is accompanied by noise. This noise will have a power spectrum encompassing many frequencies, all of which obscure the analytical signal. The frequency distribution of the noise will have different effects on a practical analysis: for our purposes, we can define *high-frequency noise* as noise that results in a poor signal-to-noise ratio for the measurement of a given sample, and *low-frequency noise* as noise that results in a poor signal-to-noise ratio for repeated measurements of a given sample. High-frequency noise is commonly treated in several fashions, including time-correlated internal standardization.¹ Low-frequency noise is often called *drift*—a slowly varying change in instrument background or sensitivity. Various filtering schemes (analog or digital) have been applied to both high² and low-frequency noise,^{3–5} with varying degrees of general applicability. Treatment of drift is most often performed by periodic reestablishment of the relationship between measured signal and chemical

composition—recalibration.⁶ Recalibration approaches demand extra time spent measuring the standard, time that would be better spent measuring samples. Presented here is a more efficient, simple, high-performance drift correction approach that should have general utility for precision chemical metrology.

It is useful here to represent the measured signal as a true signal perturbed by high- and low-frequency noise, as defined above:

$$S_{\text{measured}} = S_{\text{truth}} + \epsilon_{\text{drift}} + \epsilon_{\text{noise}} \quad (1)$$

where S_{measured} is the measured signal, S_{truth} is the true signal, ϵ_{noise} is the high-frequency noise, and ϵ_{drift} is the low-frequency noise, or drift.

In a drifting system (one dominated by low-frequency noise, $\epsilon_{\text{drift}} > \epsilon_{\text{noise}}$), time is also an enemy of the measurement; depending on the rate of drift, a “get-in-and-get-out” approach (where the experiment is designed to take as short a time as possible) may yield more robust results, since the magnitude of the drift is limited by the experiment duration. For precision measurements with well-characterized uncertainties, long integration times (a simple method for low-pass filtering) and replicate measurements are often required, demanding long experiment times. In such scenarios, system drift often puts a lower limit on the measurement precision that can be attained, either by determining the maximum permissible experiment time or by its contribution to measurement variability.

Consider an example where five samples are to be analyzed, with five replicate measurements, using an external standard approach for calibration. In a drifting system, the analyst might choose the traditional experimental design that alternates measurement of the standard and the samples, illustrated in the upper section of Figure 1. This design requires as many as 50 measurements to analyze these samples when adjacent standards are used to calibrate a given sample. Such a design compensates for drift simply by frequent recalibration. A more sophisticated use of this type of design exploits the change in response of the measurements of the standard to infer instrument response at the time the sample was measured, through some sort of interpolation. Some efficiency may be gained, with some sacrifice in responsiveness to drift, by measuring more samples between repeated measurements of the standard.

We introduce here a more efficient and effective procedure designed to be optimally responsive to system drift, which places

(1) Myers, S. A.; Tracy, D. H. *Spectrochim. Acta* **1983**, *38B*, 1227–1253.
(2) Collins, J. B.; Ivaldi, J. C.; Salit, M. L.; Slavin, W. *At. Spectrosc.* **1990**, *11*, 109–111.
(3) Rutan, S. C.; Bouveresse, E.; Andrew, K. N.; Worsfold, P. J.; Massart, D. L. *Chemom. Intell. Lab. Syst.* **1996**, *35*, 199–211.
(4) Wienke, D.; Vijn, T.; Buydens, L. *Anal. Chem.* **1994**, *66*, 841–849.
(5) Hartley, R. W. *Lab. Pract.* **1979**, *28*, 839–841.

(6) Svehla, G.; Dickson, E. L. *Anal. Chim. Acta* **1982**, *136*, 369–372.

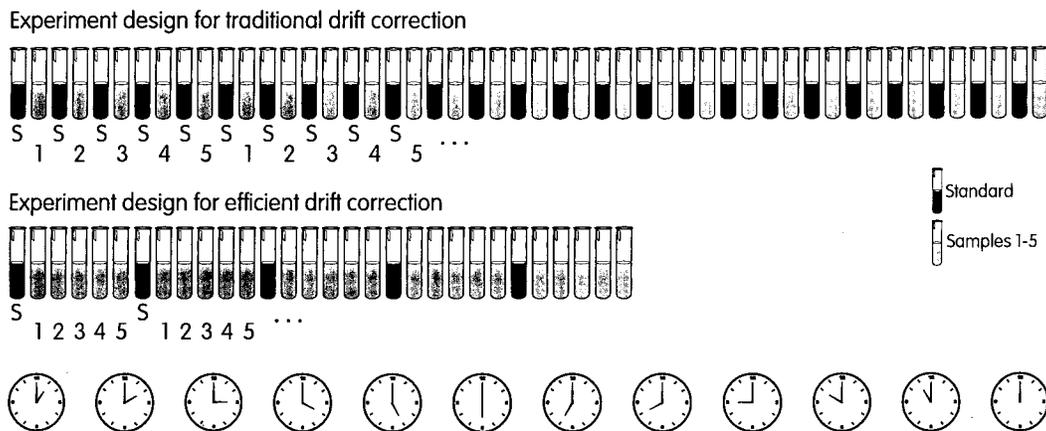


Figure 1. Experiment designs for the traditional drift correction through recalibration approach and the proposed, efficient drift correction approach.

fewer demands on the run order of samples and standards and which permits efficient distribution of measurement time for the samples and standards. A simple analysis of this procedure relies on the premise that ϵ_{drift} is some relatively smooth function of time that is independent of what samples are being measured. Equation 1 is used to estimate a time trend representing ϵ_{drift} by separating the noise sources from an estimate of S_{truth} . This estimate of ϵ_{drift} as a function of time, $\epsilon_{\text{drift}}(t)$, is then used to correct the measured data to a nominally “drift-free” condition. For each sample, the grand mean of the individual signals $S_{\text{measured}}(t)$, $\hat{S}_{\text{measured}}$, is used as the estimate of S_{truth} , and the deviations of the individual S_{measured} values from $\hat{S}_{\text{measured}}$ are used as an estimate of $\epsilon_{\text{drift}} + \epsilon_{\text{noise}}$. The separation of these noise terms is performed by fitting a smooth curve to the deviations, where the curve is the estimate of $\epsilon_{\text{drift}}(t)$, and the residuals of the fit are an estimate of ϵ_{noise} . The drift-corrected signals are calculated by adding the estimated drift, $\epsilon_{\text{drift}}(t)$, to the measured signals $S_{\text{measured}}(t)$, yielding a corrected series of signals, $S_{\text{measured}}^0(t)$.

This procedure requires that replicate measurements are performed on all samples and standards in order to obtain $\hat{S}_{\text{measured}}$, an estimate of S_{truth} . A already noted, this is a common practice when precise analytical results are desired. The fitted model of ϵ_{drift} is based on *all* the measurements, regardless of what is being measured (any standard *or* sample with sufficient a signal-to-noise ratio that the condition $\epsilon_{\text{drift}} > \epsilon_{\text{noise}}$ is met). This approach uses both the standards and the samples as diagnostics of the system drift, while the traditional approach uses only the periodic measurements of the calibration standard as the diagnostic.

The lower part of Figure 1 depicts the experiment design for our example of five samples using this more efficient drift correction approach. Not only is the experiment shorter in elapsed time, which allows less time for drift to occur, but this is a more efficient way to distribute measurement time between the samples and the standards. The flexibility permitted by this drift correction approach allows the analyst to budget more efficiently the time spent determining the calibration relationship (i.e., measuring standards) and the time spent measuring samples.

Multiplicative Drift. The discussion to this point assumes that the drift is additive—that the magnitude of the perturbation is independent of the signal level. This is typical of a system with a drifting baseline or offset. Equation 1 describes this type of drift. Equation 2 models multiplicative drift, which is dependent

$$S_{\text{measured}} = S_{\text{truth}} (1 + \epsilon_{\text{drift}} + \epsilon_{\text{noise}}) \quad (2)$$

on signal level. This is typical of a system with drifting sensitivity, or calibration curve slope. Because different samples (hence different signal levels) are being used to characterize the drift, this method requires that the signal drift be characterized as either additive or multiplicative. When the drift is additive, as presented in eq 1, it is modeled directly from the deviations. When the drift is multiplicative, as in eq 2, the deviations are mean scaled (made into relative deviations), and the drift is modeled from these relative deviations.

For multiplicative drift, we again use $\hat{S}_{\text{measured}}$ as an estimate of S_{truth} , and the mean scaled deviations, $S_{\text{measured}}/\hat{S}_{\text{measured}}$, are fitted to a smooth function, $\epsilon_{\text{drift}}(t)$, permitting the series $S_{\text{measured}}(t)$ to be corrected as in eq 3.

$$S_{\text{measured}}^0 = [\hat{S}_{\text{measured}} (1 - \epsilon_{\text{drift}}(t))] + S_{\text{measured}} \quad (3)$$

Implementation. Development of this drift correction procedure resulted from the need for a precise method for the value assignment of analyte mass fraction in single-element spectrometric solution Standard Reference Materials (SRMs). These materials are intended to be used as primary standards for calibrant preparation for determination of elemental composition. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was selected for its broad elemental coverage, relative simplicity, and performance capabilities. Our laboratory had previous, successful, experience with ICP-OES in a similar application, using a dual internal standard approach to help compensate for drift.⁷ Long experiment times are required to minimize and accurately assess uncertainties, and instrument drift is the limit to precision.

The value assignment experiment relies on the comparison of standards prepared from different source materials, under different conditions, with potentially different levels and species of impurities, in different quantities, and by different analysts. The ability to distinguish between solutions that are close in composition is directly related to the precision of the measurement, which can

(7) Beck, C. M., II; Salit M. L.; Watters, R. L.; Butler, T. A.; Wood, L. J. *Anal. Chem.* **1993**, *65*, 2899–2902.

be considered as the *concentration resolution* of the experiment. The target relative uncertainty for the value assignment is 0.3%, precision performance more typically expected from classical methods.

Though developed for ICP-OES, this method should be applicable to any system where the high-frequency noise is small enough that drift dominates the precision, allowing the drift to be well characterized. A general scheme for application of the procedure is as follows:

- (1) Design the experiment measurement run order to include repeated measurements of samples and standards that exhibit signal much greater than the detection limit.
- (2) Measure the set of samples and standards.
- (3) Select whether the drift to be corrected is additive or multiplicative (use eq 1 or eq 2).
- (4) Calculate means for each sample and standard ($\hat{S}_{\text{measured}}$).
- (5) Calculate deviations. These are calculated as $S_{\text{measured}} - \hat{S}_{\text{measured}}$ if the drift is additive, and as $S_{\text{measured}}/\hat{S}_{\text{measured}}$ if the drift is multiplicative.
- (6) Plot time series of deviations; select and fit model (for example, select order of polynomial, perform least-squares estimation). Model selection and fitting should be performed with good scientific and statistical practice.⁸
- (7) Calculate corrections for individual samples. For additive drift, these corrections are directly predicted from the fitted function $\epsilon_{\text{drift}}(t)$, and for multiplicative drift, the correction is $\hat{S}_{\text{measured}}(1 - \epsilon_{\text{drift}}(t))$.
- (8) Calculate “drift-free” time series of signals by adding corrections to measured signals, $S_{\text{measured}}(t)$.

EXPERIMENTAL SECTION

We present two examples of this drift correction procedure applied to high precision ICP-OES measurement of single-element solutions. The ICP-OES instrument used in this experiment is a Perkin-Elmer Optima 3000 XL, an axial-view ICP with solid-state array detection and an integrated Perkin-Elmer AS-91 autosampler.⁹ Data processing is performed external to the instrument software, in a spreadsheet program. All measurements are performed with time-correlated, or “real-time,” internal standardization.¹ This is made possible through the explicit selection of the integration times to be used for the measurement of the different spectral regions for the analyte and the internal standard. The concentration ratio of the analyte and internal standard must also be chosen to allow such fixed-time integration, typically selected to yield photoelectron count rates within a factor of 2 for the lines of interest and permitting high signal-to-noise ratio measurements for both signals.

The two long-duration experiments each measured six different zirconium solution samples. In each experiment, three samples are aliquots of a single solution (being evaluated for solution homogeneity) and three are different comparison standards. The experiment design employs duplicate preparations (dilution and

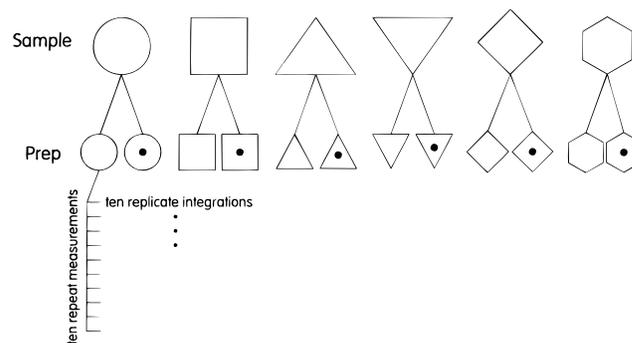


Figure 2. Schematic representation of the experiment design. The different symbol shapes denote different solutions; open and dotted symbols of the same shape are from different sample preparations. Circles, squares, and upward-pointing triangles are aliquots of a single solution, downward-pointing triangles, diamonds, and hexagons are three different solutions.

Table 1. ICP-OES Experiment Parameters and Operating Conditions

Spectroscopic Parameters	
analyte	Zr
analyte wavelength	343.823 nm
analyte excitation energy	84221 cm ⁻¹
internal standard	Y
internal standard wavelength	360.073
internal standard excitation energy	79241 cm ⁻¹
ICP Parameters	
plasma flow	15 L min ⁻¹
auxiliary flow	0.5 L min ⁻¹
nebulizer flow	0.8 L min ⁻¹
sample uptake	1 mL min ⁻¹
power	1300 W
Measurement Parameters	
signal measurement mode	peak integration, high-resolution readout
integration time	manual, 20 ms
measurement time	10 s (sum of 500 20-ms integrations)
replicate measurements	10

addition of internal standard) of each of these six solutions to permit distinction between preparation effects and statistically significant differences among the six different Zr solutions. This experiment design is schematically described in Figure 2. The shapes used here are used throughout the following figures, with the different shapes indicating the different samples and the open or dotted shape indicating the different preparations.

The solutions were prepared for analysis gravimetrically, diluting the $\sim 10 \text{ mg g}^{-1}$ Zr solutions to $\sim 10 \text{ } \mu\text{g g}^{-1}$ in two stages of about 32:1. Yttrium, used as the internal standard element for zirconium, was added at the second stage, mixed with the 2% (v/v) HNO₃ diluent, to $\sim 10 \text{ } \mu\text{g g}^{-1}$. An artifact of the gravimetric dilution procedure is that the internal standard is present at a slightly different level in each solution. However, the relative amounts of internal standard are well-known and the measured signal ratios are corrected for these differences, accounting for the mutual dilution of analyte and internal standard. The experimental parameters and operating conditions are summarized in Table 1, which has three sections describing the spectroscopic, ICP, and measurement parameters.

ICP signal quantitation was performed in “peak integration” mode, using four-pixel summation under the peak, with two-point background correction. Typical signal levels were on the order

(8) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C*, 2nd ed.; Cambridge University Press: Cambridge, 1992; Chapter 15.

(9) To adequately describe experimental procedures, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular products or equipment are necessarily the best available for that purpose.

of 1.5×10^6 to 3×10^6 counts s^{-1} , and background levels were less than 1% of the signal.

RESULTS AND DISCUSSION

The results from the two long-duration experiments are presented to illustrate the performance of the drift correction procedure and the ability, after drift correction, to detect very small differences between samples. These data are corrected for multiplicative drift, as the spectral background correction employed eliminates baseline effects.

The observed instrumental performance is well suited to this drift correction procedure because the short-term precision of the Zr/Y intensity ratio is excellent, averaging 0.02% relative standard deviation in both experiments. In the first example, the drift in the Zr/Y intensity ratio was $\pm 0.4\%$ over a period of more than 9 h. In the second example, the drift in the Zr/Y intensity ratio was $\pm 2.3\%$ over a period of more than 13.7 h.

The different panels of Figure 3 illustrate the stages of the drift correction procedure and make clear the ability to deduce different information about the samples at each stage. Figure 3a is a time trend of the measured ratios of Zr signal to Y signal, the "raw" data. See Figure 2 for the symbol descriptions. At this stage of data treatment, the variation in the ratio levels is due to the variation in both the "parent" sample and the amount of dilution (which effects both the analyte and the internal standard level). Figure 3b depicts the time trend of the Zr/Y ratios, corrected for dilution. This time trend is the S_{measured} data for this experiment. In this panel, the drift behavior is obvious, as is its sample-to-sample correlated nature. This correlation is a clear signature of instrument drift. The different levels of the different solutions are also evident, with the six solutions derived from the samples of the SRM solution clustered together (implying homogeneity) and with the preparation-to-preparation effect also evident. These same data are also summarized in Figure 4a, which shows box plots of the dilution-corrected results for the samples in this experiment, over the duration of the experiment. When assessed in this manner (or with summary statistics), the drift is sufficient to obfuscate the subtle, yet present, preparation-to-preparation effect.

Figure 3c shows the ratio of these data to their sample means, and a quartic polynomial fitted to these data. This time series is the estimate of the sum of relative perturbations, $\epsilon_{\text{drift}} + \epsilon_{\text{noise}}$, while the fitted polynomial is an estimate of ϵ_{drift} , the multiplicative drift observed in this experiment. Finally, Figure 3d displays the Zr/Y ratios corrected for both dilution *and* drift, using the multiplicative quartic model to estimate and remove drift as a function of time. These data show more clearly a preparation-to-preparation effect than the data before drift correction. Though some variability in level remains, pairwise comparisons of duplicate preparations of the same solutions exhibit the same level relationship (dotted greater than open, or vice versa). The data in Figure 3b, before drift correction, do not behave this way, rather they seem to track the drift. These data are summarized in the box plots of Figure 4b, where the narrowing of the distributions of the data is apparent in comparison to Figure 4a, as is the ability to detect the preparation effect. As a practical matter, when detectable, this preparation-to-preparation effect is the "floor" of the precision in our experiment. Further improvement in the precision of instru-

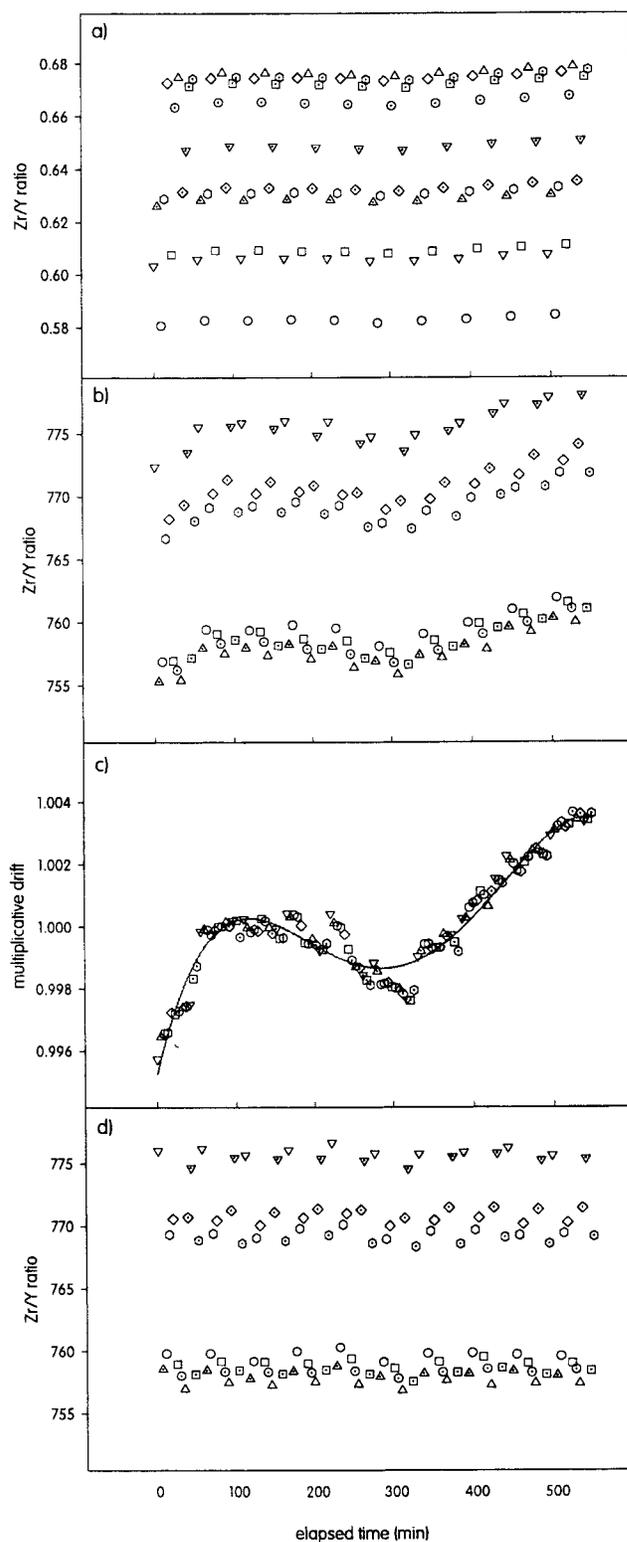


Figure 3. Data transformation through the stages of the first experiment. See Figure 2 for description of the symbols. (a) Zr/Y signal ratios as measured. (b) Zr/Y signal ratios corrected for sample dilution. (c) Noise, drift, and drift model in the Zr/Y ratios. (d) Zr/Y signal ratios corrected for sample dilution and drift.

mental measurements will not improve the precision of the analytical result. In this experiment, the precision before drift correction averages 0.059% relative standard deviation of the mean, and after drift correction, the average precision is 0.014% relative

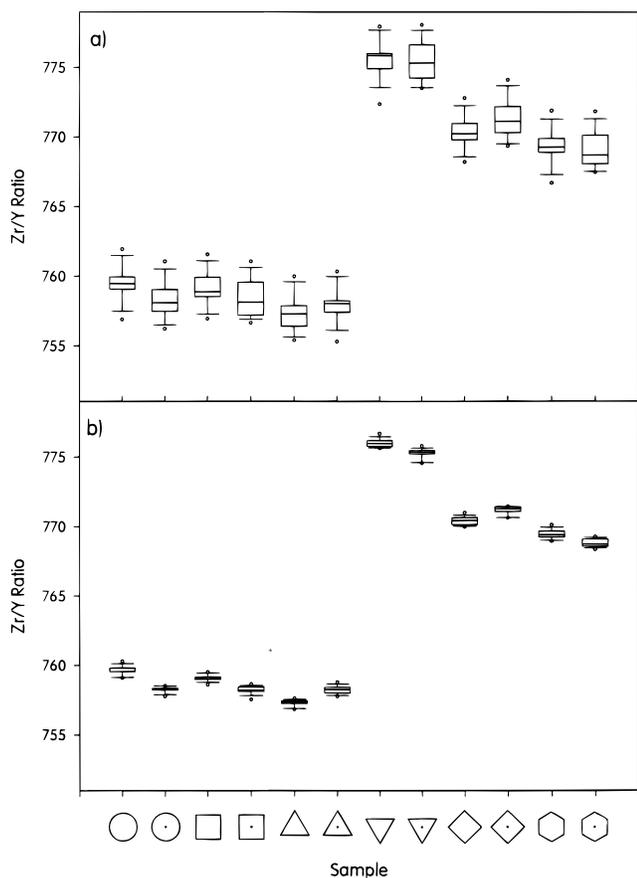


Figure 4. Box plots of Zr signal ratios for first experiment. See Figure 2 for description of the symbols. (a) Distribution of signal ratios before drift correction and (b) distribution of signal ratios after drift correction.

standard deviation of the mean. This is a more than 4-fold improvement.

A second experiment is presented in a manner identical to the first, to illustrate both a more significant drift correction improvement, and system drift of somewhat different behavior. Different preparations of the solutions were analyzed in this experiment, and the results are presented in Figures 5 and 6. Here, the drift was monotonic, and a quadratic polynomial was fitted as the model. There are missing data for several of the solutions because the solutions were consumed before the experiment ran its course. Notable in Figure 5d is the correlated fluctuation remaining in the results after drift correction. Despite this imperfect removal of system drift, significant precision improvement was attained. The precision before drift correction was 0.39% relative standard deviation of the mean, and after drift correction it was 0.031% relative standard deviation of the mean. This is a greater than 12-fold improvement.

The results in Figures 4 and 6 dramatically demonstrate the enhanced concentration resolution available when this drift correction procedure is used. More chemical information about the samples is available. Samples that would otherwise be statistically indistinguishable are now resolved into their different concentration levels.

Uncertainty Estimates. Upon careful consideration, this approach demanded examination of the uncertainty estimates for the drift-corrected data. It is to be expected that there is a sample-

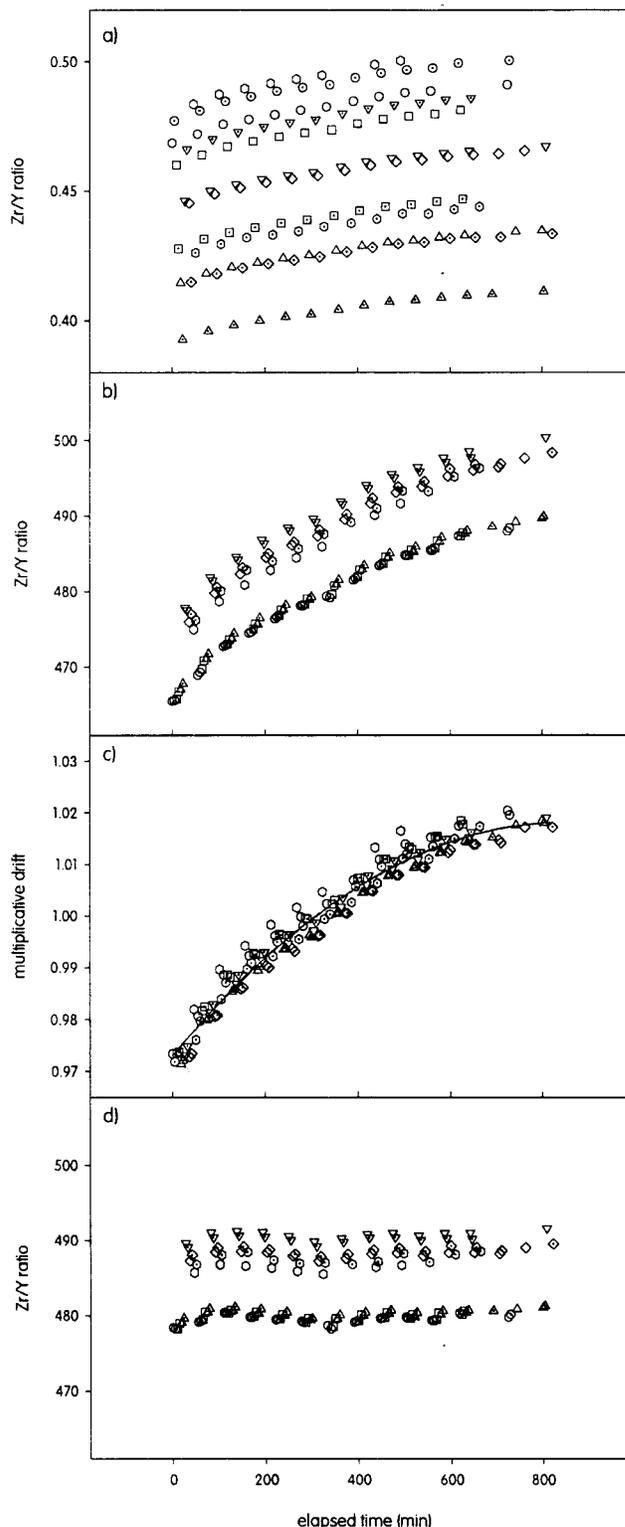


Figure 5. Data transformation through the stages of the second experiment. See Figure 2 for description of the symbols. (a) Zr/Y signal ratios as measured. (b) Zr/Y signal ratios corrected for sample dilution. (c) Noise, drift, and drift model in the Zr/Y ratios. (d) Zr/Y signal ratios corrected for sample dilution and drift.

to-sample covariance introduced by the determination of the drift correction from multiple samples. Additionally, application of the drift model uses degrees of freedom for the model parameters. A first approach to estimating uncertainty in the drift-corrected mean

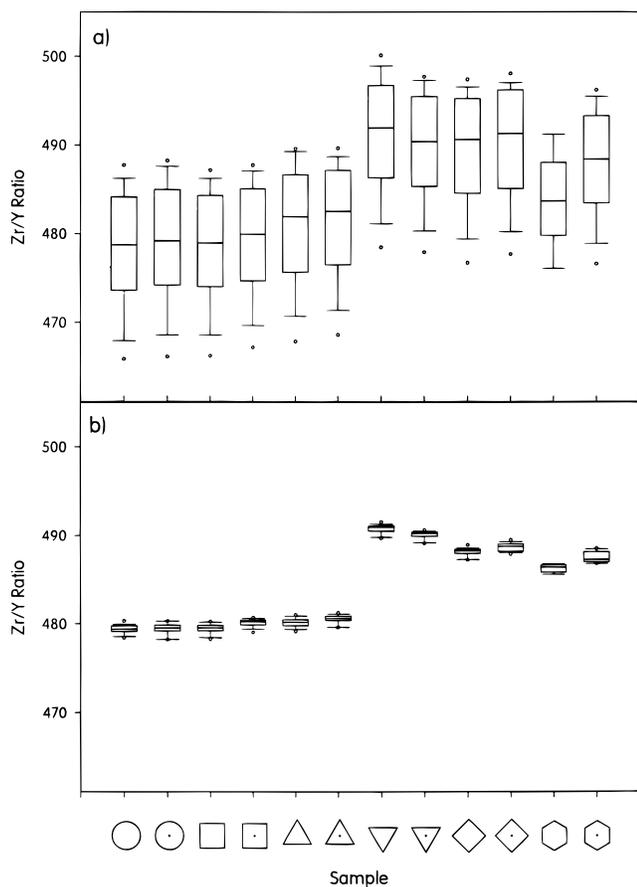


Figure 6. Box plots of Zr results for second experiment. (a) Distribution of signal ratios before drift correction and (b) distribution of signal ratios after drift correction.

will assume the covariance is negligible. This has been our experience, evidenced by the fact that the sample means show no statistically significant shifts from before to after drift correction. A heuristic approach to account for the loss of degrees of freedom is to correct the variance of the drift-corrected means.

When the variance of the mean of a sample population is estimated, the divisor used is the degrees of freedom, typically $N-1$, where N is the number of measurements. $N-1$ is used to account for the fact that the mean (used in the numerator) is determined from the data, and not independently.¹⁰ So, to estimate conservatively the standard deviation of the drift-corrected data, the degrees of freedom must be corrected by the number of parameters used in the estimate of the drift-corrected mean, now not merely the average, but in fact, dependent upon the value of a polynomial. The polynomial is determined from a large number of data, in our example cases $N = 120$. The correction for the number of parameters using a quartic polynomial drift model is a factor of $(1/120)^{1/2}/(1/115)^{1/2}$, or 1.02. So long as there are many more data than parameters used to fit the model, the correction is in fact negligible. A more statistically rigorous approach to estimating the uncertainties in the drift-corrected means, including induced uncertainty from covariance, is based on a regression approach which will be described in further work.

General Considerations. As the second experiment demonstrates, modeling the drift as a low-order polynomial is not ideal

for every experiment. We have observed simple behavior, such as that depicted here, as well as more complex behavior. Functions with many more inflection points may be required to model the observed drift in experiments of longer duration or with less stable instruments. The low-order polynomial modeling used here was selected for its intuitive clarity and its readily understood statistical treatment.

Higher-order polynomials or splines are easily computed and applied, but there is the pitfall of overfitting, and as discussed above, the use of excess degrees of freedom limits the precision improvement that can be attained. Nonparametric models are a more general solution to the drift model. Approaches such as a moving average or a more robust method such as LOWESS¹¹ are excellent candidates for drift modeling. Regardless of the modeling approach, the ability to estimate the number of fitting parameters is a requirement to properly estimate the standard deviation of the drift-corrected data.

Two other considerations are worthy of note: the time spacing of the measurements derived from the experiment run order and the effects of outliers on the drift correction. Both of these considerations have the potential to induce small biases in what is already a relatively small correction (not more than a couple of percent in the examples presented here).

Because the drift diagnostic is mean-based, the time spacing of the repeated measurements of a sample can effect the drift model. If a sample is measured more times while the instrument signal is climbing, its mean may be biased high relative to a sample that is measured more frequently while the system is drifting down. For this reason, after a run order is established for the samples to be measured (typically randomized), this same order is used for the repeated measurements from which the means are derived. This helps to ensure that sample spacing is distributed evenly over the entire experiment duration and, hopefully, evenly over the drift behavior. Subtle effects will still occur, especially if the system is drifting faster at some times than others and if there are strong slope changes in the drift behavior within the duration of a single measurement of the samples.

Outlier effects also affect the drift correction by biasing the sample means, from which the drift diagnostic is calculated. We have found the procedure to be robust with respect to outliers when there are a reasonable number of repeated measurements and samples (on the order of five repeated measurements and five samples). In these cases, the outlier effect on the sample mean and the drift model is minimized. Though we have noted outliers in our data, we have noticed no significant effects in the drift-corrected data as a result of their presence.

CONCLUSIONS

The drift correction approach presented here is effective in reducing the uncertainty of the results of a comparison of solutions with ICP-OES. The procedure is simple and should prove to be generally useful in any analytical methodology where the precision of the results is detrimentally effected by system drift. We have demonstrated that this procedure permits the use of ICP-OES at a level of precision that was previously expected only from the classical methods—titrimetry and gravimetry—or from isotope dilution measurements.

(10) Bevington, P. R.; Robinson, D. K. *Data Reduction and Error Analysis for the Physical Sciences*, 2nd ed.; McGraw-Hill: New York, 1992; p 11.

(11) Cleveland, W. S. *J. Am. Stat. Assoc.* **1979**, *74*, 829-836.

This drift correction approach is efficient and effective. It has allowed our laboratory to extend the capabilities of an existing instrumental technique, ICP-OES, to a problem that requires precision heretofore unavailable from a non-isotope-dilution instrumental measurement. Application of this approach to other techniques should yield similar enhancements.

Extension of this procedure to experimentally characterize drift as additive or multiplicative, and to adapt it to circumstances where the drift is a mix of these types, will be presented in a subsequent

study. This extension will be based on the comparison of the measured results for different dilutions of a given sample. The signal relationships for multiple dilutions will be compared to the dilution relationships, allowing the separation of additive and multiplicative components.

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