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Automated On-Line Isotope Dilution Analysis with ICP-MS Using Sandwich Flow Injection

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An automated flow injection (FI) manifold is described to perform the addition of isotopic spikes to aqueous samples on-line with ICP-MS for isotope dilution (ID) analysis. The manifold uses the sandwich technique (with the nested loop approach) to perform an injection of the isotopic spike solution within a sample (or standard) plug, the resulting sample−spike−sample sequence being pushed toward the nebulizer by a 1% HNO_3 carrier. A standard, which must contain one element not present in the spike solution to allow the determination of the dispersion coefficient, must also be used to allow a reverse isotope dilution analysis, as well as corrections for mass discrimination and/or spectroscopic interferences. Indeed, because the signals from the individual isotopes are monitored continuously, only one isotope free of spectroscopic interference is required for elements whose isotopic distribution does not vary in nature (two isotopes are still needed for the other elements), as a correction for the interference can be made by comparison with the signals from the standard. Furthermore, this automated approach makes ID-ICP-MS a faster method and does not require any preliminary analysis of the sample because the concentration profile resulting from FI allows the selection of the best isotopic ratio. It was successfully applied to the determination of Mo in saline water.

Among the various calibration strategies available with inductively coupled plasma mass spectrometry (ICP-MS), the stable isotope dilution (ID) analysis technique stands out. It is, indeed, more precise than either an external calibration[1] or the method of standard additions.[2] This feature arises because an isotope of the element being determined is used as an internal standard. Since this then constitutes the ideal internal standardization, ID will compensate for many sources of error, including sample evaporation losses and effects of concomitant elements. It has recently been demonstrated to be independent of the solvent[3] and essentially independent of instrument instability.[3,4] It is, therefore, not surprising that ID has been used for the production of certified reference materials.[5−8] It has also been recently applied to the measurement of species transformation, through the addition of species-specific isotopes.[9,10]

However, to obtain the results of best accuracy and precision, a preliminary analysis of all samples is required. The amount of enriched isotopic spikes must, indeed, be adjusted such that the resulting isotopic ratios measured for each sample correspond to the smallest error magnification factor.[2,11] Even when a nonlinear calibration is used, where stable isotopes are merged with samples or standard solutions and the resulting isotopic ratios are plotted as a function of the concentration of the standard solutions, a suitable standard concentration range must be selected.[4] Furthermore, only elements which have two isotopes free of spectroscopic interference can be determined.

Recently, we described an on-line approach, based on reversed flow injection (r-FI), for the accurate determination of naturally occurring elements, which only needed one isotope free of spectroscopic interference and did not require a preliminary analysis of the sample.[12] The approach simply involved injecting a solution of the enriched stable isotopes into a continuous flow of the sample. The concentration profile resulting from FI provided a range of isotopic ratios from which the best, in terms of error propagation, could be selected.[12]

The above approach was, however, only a proof of concept, i.e., manual injections were made into three different solutions which were used, in turn, as carrier: a blank, a standard, and the sample.[12] In particular, sample consumption is relatively high since it is pumped continuously. One way to reduce sample consumption would be to use a sandwich technique,[13] i.e., to inject the isotopic spike within a sample plug.

In this paper, we describe an automated sandwich FI manifold which can be used to perform the addition of enriched isotopes to aqueous samples on-line with ICP-MS. The sandwich technique is based on the nested loop approach of Rios et al., which they

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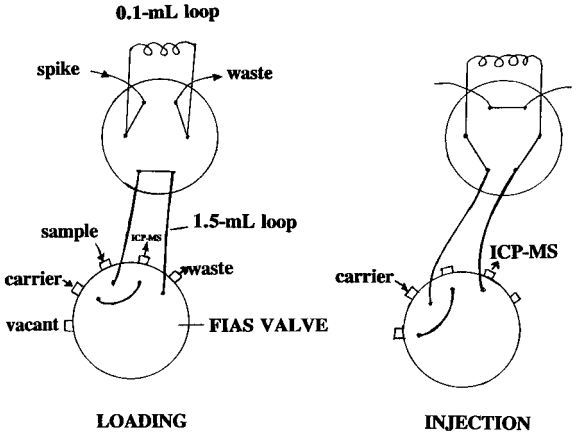

Figure 1. Schematic of the flow injection manifold. Pump 1 (not shown) of the FIAS-200 system was used to supply the sample and spike solutions, whereas pump 2 (not shown) continuously fed the carrier to the nebulizer of the ICP-MS instrument.

used for calibration purposes.[14] Like the single-line r-FI manifold,[12] the proposed approach requires only one isotope free of spectroscopic interference (for elements whose isotopic distribution does not vary in nature) and does not require a preliminary analysis of the sample. In addition, it reduces sample consumption since the isotopic spike is sandwiched within a sample plug and the blank is used as carrier. The aim of this work is to make ID-ICP-MS a faster method.

EXPERIMENTAL SECTION

Apparatus. A Perkin-Elmer/SCIEX ELAN 500 inductively coupled plasma mass spectrometer (Concord, ON, Canada) was coupled to the FI sandwich manifold illustrated in Figure 1. The manifold is composed of an FIAS-200 system (Perkin-Elmer, Norwalk, CT) in combination with an additional six-port valve (model 5020, Rheodyne Inc., Cotati, CA), which was installed on an automatic switching module (universal module, Anachem, Luton, UK) and allowed injection of isotopic spike within a sample plug. Both the FIAS-200 system and the switching module may be controlled by the ELAN-5000 software. Approximately 150 cm of 0.3-mm-i.d. Teflon tubing connected the valve to the Meinhard (C-3) nebulizer of the ICP-MS instrument.

Three modifications were made to the ICP-MS instrument: a mass flow controller was added on the aerosol carrier gas line; an $x-y-z$ translation stage was installed under the torch box; and the standard ICP-MS torch was replaced by a short ICP emission one. The operating conditions are listed in Table 1. They were obtained, while continuously aspirating a 100 μg L^{-1} solution of Li, Rh, and Pb, by optimizing daily the plasma position with respect to the interface and the aerosol carrier gas flow rate so as to maximize sensitivity. The lens settings were only adjusted if needed to equalize the Li and Pb signals, with little sacrifice in the Rh signal.

Reagents. All solutions were prepared in 1% (or 0.15 M) HNO_3 using high-purity HNO_3 (Ultrex II from J. T. Baker Inc., Phillipsburg, NJ) and deionized distilled water (Milli-Q Plus System, Millipore, Mississauga, ON, Canada). The 3 μg L^{-1} Co, Mo standard solution was prepared from 1000 mg L^{-1} monoelemental standard solutions of Co and Mo (Spex Industries, Edison, NJ). Some $NaNO_3$ (Analar grade, BDH, Toronto, ON, Canada) was also used for the 0.036 M Na solution containing 3 μg L^{-1} Mo.

Table 1. ICP-MS Operating Conditions

ICP-MS	ELAN 500
torch	PlasmaTherm
sampler and skimmer	Ni (standard)
forward rf power	1.2 kW
plasma gas	12 L min^{-1}
auxiliary gas	2.0 L min^{-1}
aerosol carrier gas	0.9 L min^{-1}
carrier flow rate	1.0 mL min^{-1}
dwell time	40 ms
sweep/reading	1
reading/replicate	1
point/spectral peak	1

Procedure. To perform an ID analysis, the two valves were first set in the loading position (see Figure 1), and pump 1 of the FIAS-200 was used to fill the 100-μL loop of the additional valve with the enriched isotope solution and the 1.5-mL loop installed on the valve of the FIAS-200 with the sample. Meanwhile, pump 2 of the FIAS-200 continuously fed 1% HNO_3 blank to the nebulizer. Pump 1 was then stopped, and both valves were switched so that the 1% HNO_3 carrier pushed the content of the two loops toward the nebulizer. The process was repeated with a standard solution instead of the sample to allow a reverse ID analysis, as well as any correction for mass discrimination and/or spectroscopic interference, to be performed.

Data Processing. Typical signals resulting from this sequence are illustrated in Figure 2. A steady 1% HNO_3 blank signal is first detected, which is followed by an increase to a fairly steady-state signal between 75 and 125 s due to the sample or standard. Positive (for the spike isotope) and negative (for the reference isotope) peaks are then observed at about 160 s, which is immediately followed by a return to the signal caused by the sample or standard at about 225 s, and finally a drop to the blank level at 330 s.

From the steady-state signal measured for the blank between 0 and 70 s, an average blank signal was computed and subtracted from all other measurements. An average natural ratio was then computed from the steady-state signals (between 75 and 125 s) of both the standard solution and the sample. Any discrepancy between the two ratios indicated a spectroscopic interference which was corrected point-by-point by subtracting from the interfered isotope S_i/D_{sample}, where S_i is the signal contributed by the interferent and D_{sample} is the dispersion of the sample into the spike. More details on this correction can be found in our previous paper, where it was clearly demonstrated.[12]

A point-by-point computation of D_{sample} was accomplished using the sandwich injection involving the standard solution containing Co in addition to Mo. Because Co is an element which was present in the standard but not the spike solution, a negative peak resulted (as in Figure 2 for ^{96}Mo), and the dispersion (shown in Figure 3) was computed by simply ratioing the steady-state signal of the standard to each point of the spike peak. As with the previous approach,[12] D_{sample} was not computed when the sample was sandwiched around the isotopic spike because any effect of concomitant element would be maximum in the steady-state

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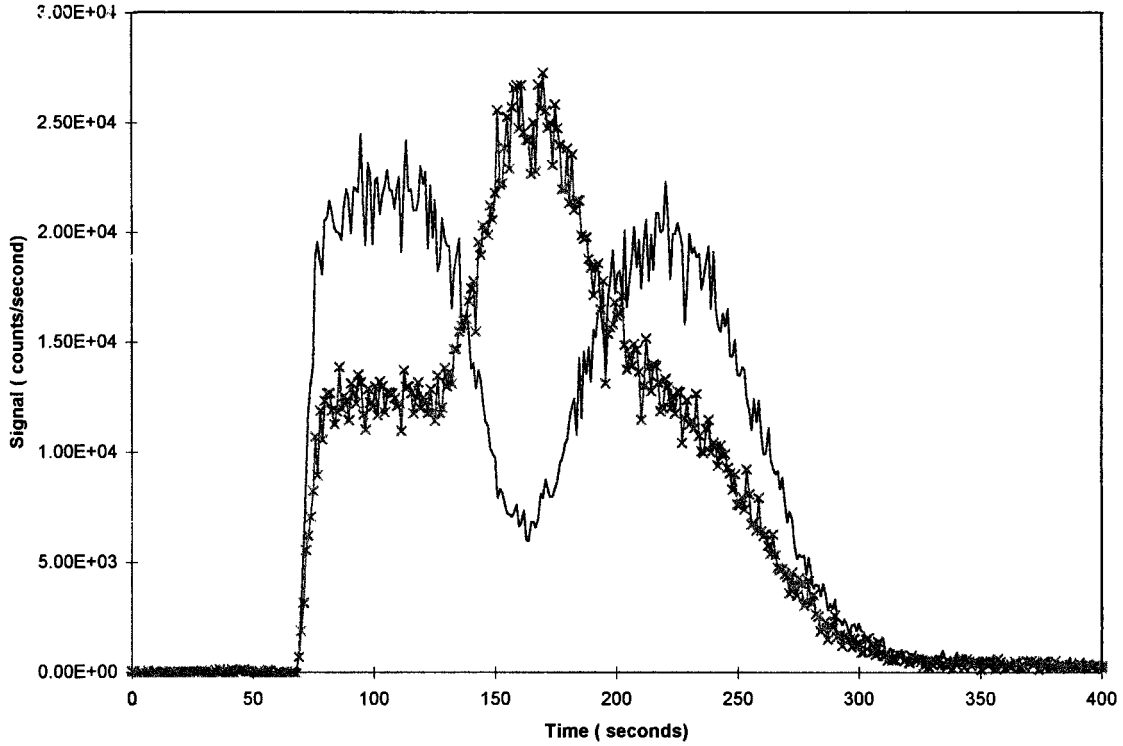

Figure 2. Signals for $^{96}Mo^{+}$ (full line) and $^{97}Mo^{+}$ (crossed line) resulting from the sandwich injection of 100 μL of 5 μg L^{-1} ^{97}Mo isotopic spike solution into 1.5 mL of 3 μg L^{-1} multielement standard, with 1% HNO_3 as carrier.

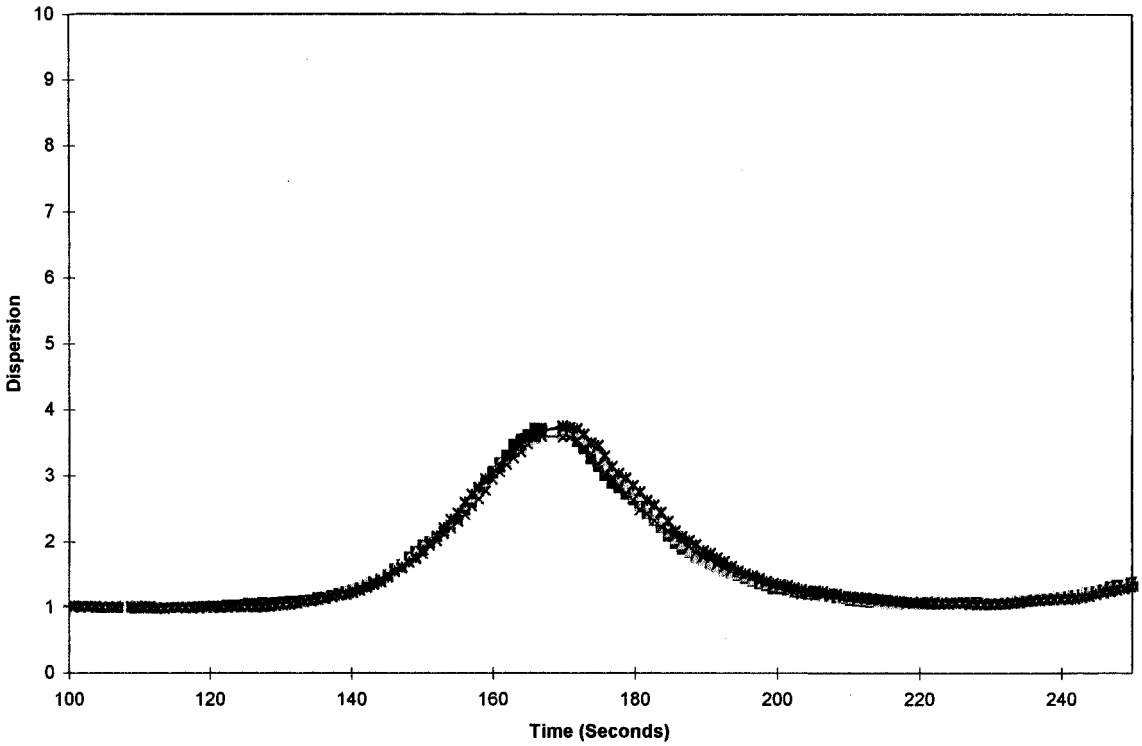

Figure 3. Dispersion profile resulting from five replicate 100-μL injections under the conditions for Figure 2.

region but would decrease during the isotopic spike injection, thereby resulting in erroneously high dispersion values during the peak.

A point-by-point computation of the ratio R (corrected, if needed, for spectroscopic interferences as described above) was then carried out. Mass discrimination was also corrected, if needed, by multiplying R by the ratio of the isotopic ratio computed from the natural abundances to that measured for the standard solution (in the steady-state region). A point-by-point computation of C_{sample} was then done using the following equation:

$$C_{\text{sample}} = (D_{\text{sample}} - 1)C_{\text{spike}}K\frac{(A' - B'R)}{(BR - A)} \qquad (1)$$

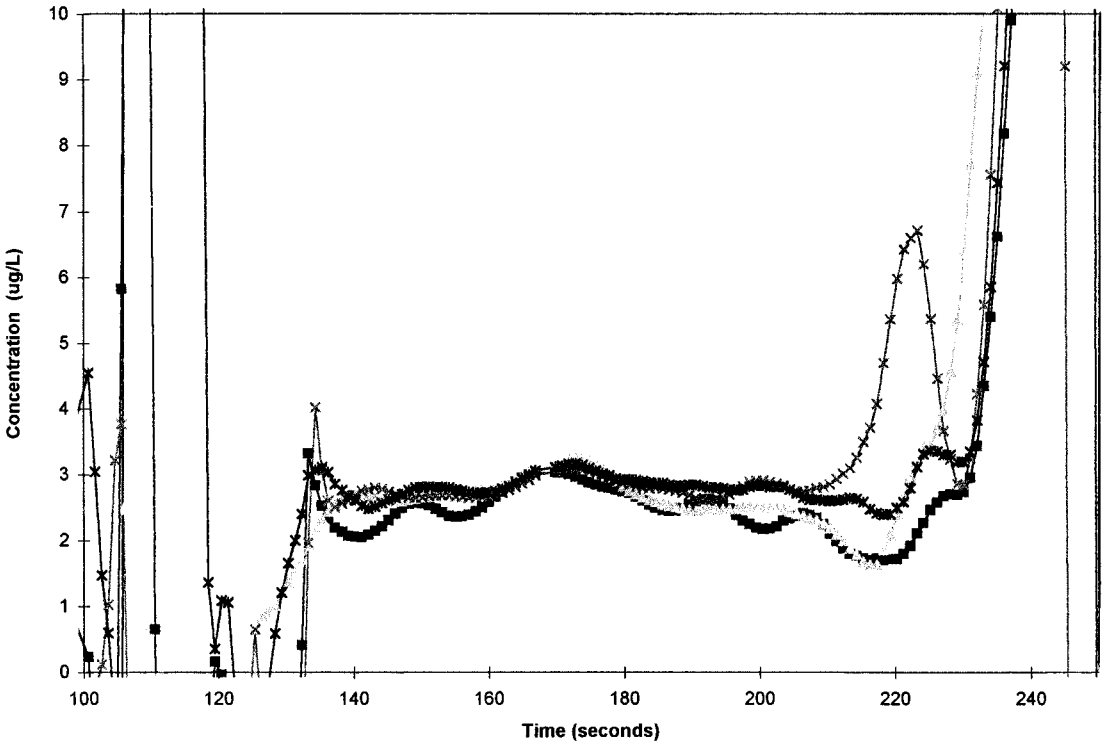

Figure 4. Result of the ID analysis of a 3 μg L^{-1} standard using a 100-μL injection of 5 μg L^{-1} ^{97}Mo isotopic spike solution. The result is obtained by computing the average over the steady concentration region.

where C_{spike} is the concentration of the isotopic spike solution which was sandwiched within the sample plug; C_{sample} is the analyte concentration (in μg L^{-1}) in the sample solution; K is the ratio of the atomic weight of the element over that of the spike; A is the natural abundance of the reference isotope; B is the natural abundance of the spike isotope; A' is the abundance of the reference isotope in the spike; B' is the abundance of the spike isotope in the spike; and R is the measured isotopic ratio (reference/spike isotopes), corrected for mass discrimination and/or spectroscopic interference. Finally, an average C_{sample} was computed in the region where a steady concentration was obtained (for instance, between 150 and 200 s in Figure 4).

RESULTS AND DISCUSSION

Comparison with the Single-Line r-FI Approach. As with the r-FI approach,[12] spectroscopic interferences can be corrected because each isotope is individually monitored (whereas with off-line ID, R is continuously measured). Furthermore, either FI approach will result in two regions where the signals for the spike and reference isotopes cross each other, as long as the concentration of the spike element is greater in the spike solution than in the sample carrier (a prerequisite which is readily achieved in trace analysis if a 5 μg L^{-1} spike solution is used). This means that a range of reference/spike isotopic ratios is obtained, thereby allowing the best ratio for a particular analysis to be selected. Under these conditions, no preliminary analysis of the sample (as must be carried out when the ID method is carried out off-line) is required.

In contrast to the r-FI approach, where the sample was used as carrier and, therefore, pumped continuously,[12] only about 2 mL of sample is required per determination (about 0.5 mL being used to rinse the loop). This reduction in sample consumption has several advantages. Aside from the obvious ones, i.e., allowing the analysis of volume-limited samples and increasing the sample throughput, memory effects are reduced as well as the rinsing time, which further increases the sample throughput. The rinsing time is, in fact, kept minimal by using the blank as carrier. As a result of this increased sample throughput, replicates can readily be carried out and pooled to improve the precision of the analysis. Compared to "off-line" ID-ICP-MS, the relative error on a single determination will, indeed, be greater when using FI, as was shown previously,[12] because the precision on the ratios depends on the measurement time which, on the other hand, had to be kept short to allow the acquisition of a sufficient number of data points across the FI peak.

A final advantage of the proposed approach over the previous one is that, because the whole process is automated with the FIAS-200, the reproducibility of injections is greatly improved, as is evident in Figure 3. There is no longer a problem in "aligning" the dispersion curve with the isotope ratio curve to compute the concentration. With the previous manual approach, the curves had to be moved, point-by-point, until the peaks would overlap. This was, needless to say, tedious and is no longer required with the proposed approach.

Determination of Mo in Saline Water. A comparison of precision was made under the presence of important nonspectroscopic interferences. Four replicate analyses of two 3 μg L^{-1} solutions of Mo, one in 0.036 M $NaNO_3$ and one in 1% HNO_3, were carried out using a 5 μg L^{-1} ^{97}Mo spike solution, with ^{96}Mo as the reference isotope. The individual and pooled results are summarized in Table 2 and compared with the individual results obtained by the previous r-FI approach. For the comparison to

Table 2. Concentrations (in μg L^{-1} ± 1 Standard Deviation) Found in 3 μg L^{-1} Mo Solutions

matrix	single (r-FI[12])	single (this method)	pooled (this method)
1% HNO_3	3.06 ± 0.22	2.96 ± 0.19, 3.05 ± 0.07, 3.05 ± 0.04, 3.12 ± 0.08	3.05 ± 0.07
0.036 M Na	3.01 ± 0.26	2.96 ± 0.13, 2.98 ± 0.08, 2.99 ± 0.15, 2.99 ± 0.09	2.98 ± 0.01

be fair, the average Mo concentration for each result was computed over a 20-s window as had been done with r-FI.[12]

Although the accuracy is similar, a slight improvement in the precision of individual results was achieved with the proposed method, probably because matching the dispersion curve to the ratio profile is no longer dependent on the reproducibility of the injection, as discussed above. Furthermore, the precision of the pooled results is clearly improved.

CONCLUSION

The proposed sandwich FI-ID approach, therefore, makes ID analysis as simple as an external calibration but with the added accuracy and precision associated with ID analysis. No preliminary analysis of the sample is needed. In addition, the spiking is done on-line in a closed system, which minimizes contaminations and eliminates the time-consuming disadvantage of ID. Furthermore, reduced sample consumption results from the discrete sample injection performed. This, in turn, minimizes memory effects and reduces the rinsing time, which leads to a higher sample throughput. Similarly, because only discrete injections of the spike solution are made, isotopic carryover is minimized, as both the sample itself and especially the carrier act as washing solutions. Finally, this approach broadens the range of applications of ID-ICP-MS since it requires only one isotope free of spectroscopic interference for all elements whose isotopic distribution does not vary in nature.

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