The CETAC ADX-500 Autodiluter System: A Study of Dilution Performance With the ELAN 6000 ICP-MS and ELAN Software

Thomas W. May and Ray H. Wiedmeyer
U.S. Geological Survey, Biological Resources Division
Columbia Environmental Research Center
4200 New Haven Road, Columbia, MO 65201 USA

ABSTRACT

The CETAC ADX-500 autodiluter system was tested with ELAN® v 2.1 software and the ELAN 6000 ICP-MS instrument to determine on-line automated dilution performance during analysis of standard solutions containing nine analytes representative of the mass spectral range (mass 9 to mass 238). Two or more dilution schemes were tested for each of 5 test tube designs. Dilution performance was determined by comparison of analyte concentration means of diluted and non-diluted standards. Accurate dilutions resulted with one syringe pump addition of diluent in small diameter round-bottomed (13 mm OD) or conical-tipped (18 mm OD) tubes and one or more syringe pump additions in large diameter (28 mm OD) conical-tipped tubes. Inadequate dilution mixing which produced high analyte concentration means was observed for all dilutions conducted in flat-bottomed tubes, and for dilutions requiring multiple syringe additions of diluent in small diameter round-bottomed and conical tipped tubes. Effective mixing of diluted solutions was found to depend largely upon tube diameter and liquid depth: smaller tube diameters and greater liquid depth resulted in ineffective mixing, whereas greater tube diameter and shallower liquid depth facilitated effective mixing. Two design changes for the autodiluter were suggested that would allow effective mixing to occur using any dilution scheme and tube design.

INTRODUCTION

ICP-MS is a versatile analytical tool having a wide variety of research applications and routine use in numerous application fields, such as environmental analysis, geochemistry, biological materials, and semiconductor operations. While the ICP-MS technique offers fast multielement analysis, excellent detection power, automation, and flexibility, it poses special challenges in areas such as sample preparation, matrix induced space charges, and spectral interferences (1). The cones, lens, and detector components of the ICP-MS are especially sensitive to undesirable matrix components, such as excessive ion concentrations (Al, Na, K, Ca, Mg, Fe, etc.), high dissolved solids, and carbon from incompletely digested samples (2). One of the easiest approaches to reduce matrix component effects is to employ sample dilution in preparing samples for ICP-MS analysis. By diluting samples, the analyst can reduce exposure of the ICP-MS components to undesirable matrix constituents, thus also reducing the frequency of instrumental maintenance and service. Fortunately, the superior detection limits and sensitivity achievable with ICP-MS for most elements allows for the routine use of sample dilution to alleviate some of these matrix problems.

In various application fields, especially environmental analysis, samples are often of widely varying matrix constituency and unknown elemental composition. Such samples have to be diluted and scanned on the ICP-MS (e.g., semi-quantitative scan) to determine appropriate dilution factors for the analytes of interest in each sample. Just as importantly, the results of the scan help to identify analytes that are appropriate to serve as internal standards and samples suitable for analytical duplicates, dilutions, and spikes, in accordance with the required quality control (QC) protocols specified in U.S. Environmental Protection Agency (EPA) Methods 200.8 and 6020 (3-4). After scanning, the properly diluted samples and associated QC samples can be arranged in the autosampler trays in preparation for the final quantitative analysis run. Conventionally, such predilution of samples is accomplished by manual dilution procedures, which can be time-consuming and tedious work that is prone to human error as well as sample contamination. Commonly recognized errors associated with manual dilution procedures include incorrect sample/diluent volumes, wrong pipette or pipette settings, contaminated pipette tips, contaminated diluent, and calculation errors.

On-line automated dilution for ICP-MS has been previously described using flow-injection analysis ICP-MS (FIA-ICP-MS) (5). FIA-ICP-MS allows for on-line dilution and reagent addition through a 5- or 8-port switching valve and associated injection loops. The

8-port valve configuration allows for two injection loops, one for the sample and a second for diluents, with the dilution factor being defined by the volumes of the injection loops. The major problem with using FIA-ICP-MS for sample dilution is its lack of versatility, i.e, only one dilution factor can be assigned for all samples in the analytical run. If some samples require further dilution, this must be accomplished in additional analytical runs by changing injection loop volumes on the FIA port valve. Recently, CETAC (CETAC Technologies Inc., Omaha, NE USA) introduced a uniquely designed autodiluter unit, the ADX-500, which is based on its ASX-500 autosampler. Perkin-Elmer SCIEX Instruments (Concord, Ontario, Canada) has incorporated this autodiluter into version 2.1 of the ELAN® software, enabling use of the CETAC system by the ELAN 6000 ICP-MS. This ADX-500 autodiluter has the potential of bringing a new level of simplicity and automation to ELAN 6000 ICP-MS analysis that can markedly reduce sample setup time and error. However, there is no existing performance information on this diluter system. It is the purpose of this study to evaluate the dilution performance of the CETAC ADX-500 autodiluter system used in conjunction with the ELAN 6000 ICP-MS and associated ELAN software.

Description of Dilution Equipment and Software Application

The ADX-500 autodiluter, formerly the ADX-100, comprises an L-shaped dilution device which sits on top of the autosampler, thus not appreciably increasing the footprint of the autosampler. The autosampler has two sampling arm probes. The sample probe introduces undiluted or diluted sample to the peristaltic pump, as would occur with any autosampler. The dilution probe, however, is connected to a 5-mL glass syringe equipped with a plunger and switching valve. When dilution is called for, the dilution probe enters the sample solution, withdraws a calculated volume and places it in an empty "dilution" tube, the position of which is software specified. A switching valve then changes to allow diluent to be pumped on top of the sample, the volume of which is set by the software specified dilution factor. If the syringe pump addition of diluent is the final one for completing the dilution, the dilution probe moves slowly upward from the bottom of the tube as it dispenses the diluent. Any mixing of the sample and diluent must be accomplished by the force of the liquid being dispensed from the syringe pump accompanied by this vertical (upward) probe movement, as there is no stirring-type action associated with either probe. The dilution probe, syringe plunger, switching valve, and transfer line are all Teflon® components. The sample contacts only the transfer line, which can contain up to 1.3 mL of undiluted sample.

The ELAN v 2.1 software accommodates the autodiluter in the sampling page of the method window by introducing new fields: Dilution Factor, Dilution to Volume (mL), 1st Dilution Position, and Probe Purge Position (6). The software allows for selection of the CETAC ADX-500* autodiluter as well as a variety of corresponding tube racks. The new fields are activated when the ADX-500 is selected as the sampling device to be used. The "1st Dilution Tube Position" refers to the tube position in the autosampler rack where the first dilution will take place. Subsequent dilutions use the next available tube in sequence from this initial position. Sequencing can be maintained if different methods are loaded in the batch page of the sample file by placing "0" in the "1st Dilution Tube Position" for all method files called up subsequent to the starting method file. The "Probe Purge Position" refers to the autosampler tube position where the autodiluter probe, transfer line, and syringe are flushed and filled with fresh diluent prior to blank analysis. This flushing or priming of diluter components occurs whenever a method file specifying the autodiluter is loaded as the active method. When the ELAN QC Checking features are enabled, the Sample pane of the method window contains one additional entry in the "Action" column of the Upper Limit field: Wash for X, dilute, and rerun current. For this action to have priority over other QC actions, "Sample Limits" in the QC Action Controls pane of the Method window must be set to the highest priority (priority 1). Samples that exceed the entered upper limit for a particular analyte mass (usually the highest calibration standard concentration for each element) are diluted according to the global dilution factor specified in the Sampling pane of the method window. The sample will continue to be sequentially diluted with this dilution factor until the concentration for each analyte falls within the upper limits as indicated in the sample pane of the method window. Entries in the "Measurement Action (*)" column of the sample batch page of the sample window for autosampler setup include the options: Run Blank, Standards, and Diluted Sample; Run Diluted Sample; Run Blank and Diluted Sample; and Run Standards and Diluted Sample. These options can be used to automatically predilute samples for either semi-quantitative or quantitative analysis. Thus, samples can be prediluted if desired and then, based on a QC check, further serially diluted using a global dilution factor until all analytes are within specified upper concentration limits. However, predilution

**Note: The ADX-500 appears in v 2.1 of the ELAN software as the ASX-500/ADX-100.*

cannot be used with samples designated as QC in the "Sample Type" column of the batch page of the sample file, i.e., QC spike, QC duplicate, QC dilution, etc. A predilution command for these samples will be ignored and dilution will not be performed. Because of the high versatility of the ELAN software, different method files can be loaded in the same batch page of the sample window while maintaining instrument calibration, which allows the autodiluter to be turned off where dilution is not desired (e.g., for running Method 6020 QC samples), and then turned back on again, all while maintaining dilution tube sequencing. Global dilution factors may be varied on a sample basis by assigning different methods for the analysis of specific samples.

EXPERIMENTAL

Instrumention

All experimental runs were conducted with an ELAN 6000 ICP-MS equipped with a Gilson® peristaltic pump (Model M312), a cyclonic spray chamber, and a Meinhard® TR-30-C3 nebulizer. Pump speed was a constant 10 rpm, sample flush delay 65 sec, read delay 30 sec, and wash 80 sec. Timing page parameters were: 20 sweeps/read, 1 read/replicate, 3 replicates, peak hopping mode, 50 msec dwell time, 1 sec total integration time. The instrument's tuning, pulse voltage, analogue voltage, dual detector calibration, and auto lens were all optimized according to the manufacturer's specifications (6). Nebulizer gas flow was optimized to result in Ba^{++}/Ba^{+} and CeO^{+}/Ce^{+} <3%. Analytes were monitored that were representative of low, mid, and high masses: Be^{9}, Al^{27}, V^{51}, Ni^{60}, Zn^{66}, As^{75}, Mo^{98}, Cd^{114}, Tb^{159}, Pb^{208}, U^{238}. Internal standards, which were metered into the sample line via peristaltic pump included 50 ppb Ge (Be, Al, V, Ni, Zn, As), 10 ppb Rh (Mo, Cd), 10 ppb Tm (Tb), and 10 ppb Bi (Pb, U). Three standards constituting the calibration line for each analyte were made from multiple element stocks (High Purity Standards, Charleston, SC USA) to final concentrations of 10 ppb, 20 ppb, and 40 ppb. Calibration verification was monitored throughout analytical runs by use of an independent calibration verification standard (Claritas PPT, Spex Industries, Metuchen, NJ USA) at a concentration of 25 ppb. Test solutions were delivered to the ICP-MS by means of a CETAC ADX-500 autodiluter system.

Autodiluter Testing Procedure

A major concern of diluter performance was its solution mixing capability, i.e., whether the action or force of diluent being delivered by the syringe pump was adequate enough to properly mix the diluted sample. The peculiar action of moving the autodiluter probe upward in the tube as the final syringe pump addition of diluent is dispensed was presumably designed to facilitate sample-diluent mixing. It was suspected that this liquid mixing capability could be influenced by tube geometry and by the number of aliquots of diluent delivered by the syringe pump. Thus, the diluter tests were designed to investigate different tube designs and dilution schemes. Two multiple element testing solutions containing the analytes of interest were prepared at concentrations of 25 ppb and 250 ppb. Each dilution test consisted of ten analyses: five analyses of the 25 ppb solution (undiluted) and five analyses of a 10X dilution of the 250 ppb solution, with all analyses conducted in a random fashion. Each test focused on a specific tube design and tested two different 10X dilution schemes, one requiring only one addition of diluent from the syringe pump, and the second requiring two or more additions of diluent from the syringe pump. Tube sizes and dilution schemes tested are indicated in Table I. The tubes tested utilized three of the four tray sizes available for the ADX-500 autodiluter (tubes for tray D, maximum tube diameter of 25 mm, were not tested). The dilution schemes tested required from 1 to 6 syringe pump additions of diluent.

Statistical Testing

The data were analyzed as a 2 X 11 factorial arrangement of treatments (2 = concentration levels of 25 ppb (undiluted) and 250 ppb (autodiluted 10X), and 11 = 11 different dilution tests). For each dilution test (treatment), means were computed for each analyte for the undiluted samples (n = 5) and for the autodiluted samples (n = 5). An overall concentration mean (n = 5 analyses x 11 analytes) was also computed for each of the undiluted and diluted samples in a dilution test. Concentration means for undiluted and diluted samples in each tube type and dilution scheme were compared to determine significant differences. Mean differences (HO: LSMEAN1 = LSMEAN2) were ascertained using Fisher's least significant difference or LSD (7).

Results and Discussion

Overall concentration means are presented in Table II. Mean percent differences were ≤4 for five of the 11 dilution tests: 17 mm OD RBPP, 0.5 mL to 5 mL; 18 mm OD CTPP, 0.5 mL to 5 mL; and 28 mm OD CTPP, all three dilution schemes. For the remaining sixdilution tests, mean percent differences ranged from 5 to 16, with the means for autodiluted samples always being high relative to those for undiluted samples. Precision measured by the overall average of concentration mean relative standard deviations (%RSDs, n = 3 replicates of 1 reading for each analyte) were comparable, ranging from 2.4 to 3.5, except for dilution tests where autodilution was involved

TABLE I
Tube Sizes and Dilution Schemes Used for Autodilutor Performance Tests

Tube Description	Approximate Capacity (mL)	ADX-500 Tray	Dilution Schemes and Required Syringe Pump Additions ( )
17 mm OD round-bottomed polypropylene (RBPP)	12	B	0.5 mL to 5.0 mL (1); 1.0 mL to 10.0 mL (2)
18 mm OD screw capped conical tipped polypropylene (CTPP)	15	B	0.5 mL to 5.0 mL (1); 1.0 mL to 10.0 mL (2)
13 mm OD round-bottomed polypropylene	8	A	0.5 mL to 5.0 mL (1); 0.7 mL to 7.0 mL (2)
13 mm OD mm flat-bottomed polypropylene (FBPP)	7	A	0.5 mL to 5.0 mL (1); 0.7 mL to 7.0 mL (2)
28 mm OD screw capped conical tipped polypropylene	50	E	0.5 mL to 5.0 mL (1); 1.0 mL to 10.0 mL (2); 3.0 mL to 30 mL (6)

TABLE II
Concentration Means (ppb) and RSDs From Autodilutor Performance Tests

Tube Type	Standard Used[a]	Dilution Scheme	Measured Conc Mean[b]	Measured Mean % Diff	Measured Conc RSD Mean[c]
17 mm OD RBPP	25 ppb	undiluted	25.64	< 1	2.4
	250 ppb	0.5 mL to 5 mL	25.58		2.7
	25 ppb	undiluted	24.81	11	2.9
	250 ppb	1.0 mL to 10 mL	27.95		3.3
18 mm OD CTPP	25 ppb	undiluted	24.91	4	2.8
	250 ppb	0.5 mL to 5 mL	25.00		3.0
	25 ppb	undiluted	24.74	9	2.9
	250 ppb	1.0 mL to 10 mL	27.19		3.0
13 mm OD RBPP	25 ppb	undiluted	25.23	16	2.9
	250 ppb	0.5 mL to 5 mL	29.88		18.
	25 ppb	undiluted	25.64	5	3.1
	250 ppb	0.7 mL to 7 mL	26.98		3.5
13 mm OD FBPP	25 ppb	undiluted	24.96	13	2.8
	250 ppb	0.5 mL to 5 mL	28.64		17.
	25 ppb	undiluted	25.33	12	3.1
	250 ppb	0.7 mL to 7 mL	28.92		5.5
28 mm OD CTPP	25 ppb	undiluted	25.29	<1	2.4
	250 ppb	0.5 mL to 5 mL	25.32		2.7
	25 ppb	undiluted	25.34	<1	2.8
	250 ppb	1.0 mL to 10 mL	25.51		3.0
	25 ppb	undiluted	26.03	<1	2.7
	250 ppb	3.0 mL to 30 mL	25.89		2.9

[a] *25 ppb and 250 ppb standard solutions prepared using standards from High Purity Standards, Charleston, SC USA.*
[b] *Concentration (ppb) mean computed from analyses X 11 analytes (n=55).*
[c] *Concentration RSDs (ppb) computed from 5 analyses X 11 (n=55).*

using 13 mm OD RBPP and 13 mm OD FBPP tubes with 0.5 mL to 5 mL dilution schemes. In these tests, precision was considerably worse (17 and 18 %RSD). Precision averaged 5.5 and was ~2X to ~4X higher (worse) for most masses with autodilution involving the 13 mm OD FBPP tubes and the 0.7 mL to 7 mL dilution scheme.

Statistical testing results for analyte concentration means (Fisher's LSD) by individual mass and for all masses in a specified tube and dilution scheme (overall means) are presented in Table III. Overall means and individual mass means were significantly different ($p = 0.0001$ to 0.0007) for 6 of the 11 dilution tests. There was no significant difference between overall means and individual mass means for the following dilution tests : 17 mm OD RBPP, 0.5 mL to 5 mL dilution scheme; 18 mm OD CTPP, 0.5 mL to 5 mL; 28 mm OD CTPP, all dilution schemes. The one exception was for Zn^{66} with the 18 mm OD CTPP tube and 0.5 mL to 5 mL dilution scheme ($p=0.002$), which was likely caused by contamination of the 250 ppb stock solution for this analyte (Table III).

It was suspected that significant concentration mean differences in 6 out of 11 diluter tests were due to inadequate sample-diluent mixing. The syringe pumping speed of the ADX-500 is factory preset, thus liquid is pumped into any dilution tube with the same force. This liquid force plus the upward probe movement during the final syringe pump diluent addition were supposed to completely mix the sample-diluent solution. However, tube geometry and liquid column diameter and depth can greatly influence whether the liquid force and vertical probe movement can produce effective sample-diluent mixing. Thus, the success of a dilution scheme with the ADX-500 was found to depend on tube geometry, liquid column depth, and the number of syringe pump additions. For example, dilution schemes with one and two syringe pump additions in flat-bottomed tubes (FBPP) failed to produce statistically equal mean concentrations for each of the 11 masses tested (Table III). These results, combined with the higher concentration mean RSDs (17 and 5.5, Table II), suggested a solution mixing problem, presumably due to the original sample liquid being inadequately flushed out of the corner spaces at the tube bottom by diluent from the syringe pump addition. This resulted in higher concentrations in the bottom or lower portion of the tube and corresponding elevated analyte concentration means because the sample probe draws liquid from the bottom of the tube. To overcome this problem, one simply has to use round-bottomed tubes. However, while single syringe pump additions in either 17 mm OD RBPP or 18 mm OD CTPP tubes produced statistically equal means (Table III), two syringe pump additions in the same tubes did not, again suggesting a solution mixing problem. The resulting concentration means were always high (9% and 11%, Table II), indicating that a concentration gradient was being formed similar to that in the FBPP tubes, with higher concentrations at the tube bottom than at the top of the liquid column. The liquid column depth in these tubes was such that two syringe pump additions of diluent could not be adequately mixed with the sample by liquid force and autodiluter probe movement. To confirm this hypothesis, two tests were conducted with the 17 mm OD RBPP tube. In the first test, the 1.0 mL to 10 mL dilution scheme was repeated, which in the initial test produced statistically unequal concentration means (24.81 vs 27.95, 11% mean difference, Table II). However, once the 10X autodilution was made on the 250 ppb solution by the ADX-500, the run was aborted and the resulting liquid column manually shaken. This process was repeated for each of five dilutions. Overall concentration means (25 ppb vs 250 ppb diluted 10X) were virtually identical (25.34 ppb vs 25.46 ppb), confirming that inadequate mixing was the source of the initial concentration mean difference. A second test involved manually introducing an Ar gas probe into the dilution tube following the movement of the autodiluter probe. It was thought that the constant stream of bubbles would create eddy currents to facilitate mixing. As in the first test, the overall concentration means were virtually identical (25.34 ppb vs 25.53 ppb), suggesting that a constant bubble stream was successful in mixing the dilution solution in the 17 mm RBPP tubes. In contrast, all dilution schemes utilizing 1 to 6 syringe pump additions in 28 mm OD CTPP tubes were adequately mixed as evidenced by statistically equal means (Table III). These results indicate that increasing liquid column diameter and shallow depth greatly facilitate sample-diluent mixing under the design constraints of the ADX-500. Presumably, the increased diameter allows for greater turbulence and eddy current mixing than can occur in longer and narrower liquid columns, and such increased turbulence was visibly evident. Fifty-mL tubes (28 mm OD), however, may not be practical for routine use, because the number of tubes that can be accommodated in the autosampler racks (n = 84) would only suffice for smaller sample sets, especially in light of Methods 200.8 and 6020 QC requirements.

In light of dilution test results, several design changes can be suggested for the ADX-500 autodiluter system that will facilitate mixing of the dilution tube solution, thereby enabling the system to accommodate more tube types and dilution schemes.

TABLE III
Mean Comparison Statistics for ADX-500 Autodiluter Dilution Tests

Tube Type	Dilution Scheme	Be^{9}	Al^{27}	V^{51}	Ni^{60}	Zn^{66}	As^{75}
17 mm OD RBPP	0.5 mL to 5 mL	0.810b	0.333	0.938	0.786	0.446	0.834
	1.0 mL to 10 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
18 mm OD CTPP	0.5 mL to 5 mL	0.187	0.796	0.505	0.692	0.002	0.352
	1.0 mL to 10 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
13 mm OD RBPP	0.5 mL to 5 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
	0.7 mL to 7 mL	0.0001	0.0003	0.0001	0.0001	0.0001	0.0001
13 mm OD FBPP	0.5 mL to 5 mL	0.0003	0.0004	0.0002	0.0001	0.0001	0.0002
	0.7 mL to 7 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
28 mm OD CTPP	0.5 mL to 5 mL	0.936	0.868	0.692	0.228	0.507	0.600
	1.0 mL to 10 mL	0.678	0.138	0.163	0.215	0.502	0.846
	3.0 mL to 30 mL	0.782	0.433	0.850	0.577	0.157	0.400

Tube Type	Dilution Scheme	Mo^{98}	Cd^{114}	Tb^{159}	Pb^{208}	U^{238}	Overall Means[a]
17 mm OD RBPP	0.5 mL to 5 mL	0.352	0.355	0.702	0.445	0.888	0.837
	1.0 mL to 10 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
18 mm OD CTPP	0.5 mL to 5 mL	0.628	0.231	0.715	0.644	0.629	0.737
	1.0 mL to 10 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
13 mm OD RBPP	0.5 mL to 5 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
	0.7 mL to 7 mL	0.0001	0.0003	0.0132	0.0001	0.0001	0.0001
13 mm OD FBPP	0.5 mL to 5 mL	0.0001	0.0001	0.0006	0.0003	0.0007	0.0001
	0.7 mL to 7 mL	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
28 mm OD CTPP	0.5 mL to 5 mL	0.935	0.346	0.682	0.942	0.404	0.918
	1.0 mL to 10 mL	0.678	0.138	0.715	0.446	0.838	0.548
	3.0 mL to 30 mL	0.782	0.433	0.868	0.513	0.558	0.613

[a] *Probability of > T (HO: LSMEAN1=LSMEAN2); n=55 (5 analyses X 11 analytes, 25 ppb); n=55 (5 analyses X 11 analytes, 250 ppb autodiluted 10X).*
[b] *Probability of > T (HO: LSMEAN1=LSMEAN2); n=5 analyses 25 ppb; n=5 analyses 250 ppb autodiluted 10X).*

One approach is to rapidly oscillate the autodiluter probe as it remains in the solution after dilution by using the stepper motor that controls sampling arm movement (8). Such rapid probe action effectively stirs the entire diluted tube contents. Another possibility is to incorporate a gas line into the autodiluter probe design, such that a stream of Ar bubbles would emanate from the vicinity of the probe tip while the syringe pump additions of diluent were being added. The manual addition of such an Ar gas line was described above and did result in effective mixing of the diluted solution.

CONCLUSION

The CETAC ADX-500 autodiluter system was investigated for its dilution performance with the ELAN 6000 ICP-MS and ELAN v 2.1 software. New functionality in the ELAN v 2.1 software supports the autodilution system, allowing intelligent on-line dilution during the analytical run. The testing of various dilution schemes and tube types indicated problems with adequate mixing of diluted solutions. Accurate dilution results were achieved from dilutions using single syringe pump additions in 17 mm OD round-bottomed tubes and 18 mm OD conical-tipped tubes. Dilutions requiring single or multiple syringe pump additions in flat-bottomed 13 mm OD diameter tubes could not be effectively mixed by the combination of liquid

force and vertical probe movement. Ineffective mixing also occurred with dilutions requiring multiple syringe pump additions in 17 mm OD round-bottomed tubes and 18 mm conical-tipped tubes. Good dilution results were achieved in 50-mL conical-tipped tubes with dilution schemes requiring 1 to 6 syringe pump additions. Given the design constraints of the ADX-500 diluter, effective mixing was found to depend largely upon tube diameter and liquid depth: smaller tube diameters and greater liquid depth results in ineffective mixing, whereas greater tube diameter and shallower liquid depth enhances effective mixing. In this study, ineffective mixing resulted in analyte concentration means that were high by 9% to 16%. Incorporation of a stirring-type action in the autodiluter probe movement or the addition of Ar gas entrainment could be used to improve mixing performance in 13 mm OD, 17 mm OD, and 18 mm OD tubes used for testing in this study.

As a result of these findings, our laboratory uses either 17 mm OD RBPP or 18 mm CTPP tubes on a routine basis with dilution schemes that require only one syringe pump addition of diluent. This combination gives the accuracy and precision required for predilution, semiquantitative, and quantitative analytical purposes. Each laboratory should evaluate their data quality needs and desired dilution schemes for accuracy and precision before using any autodilution system.

Received July 28, 1998.

REFERENCES

1. E. H. Evans and J. J. Giglio, *J. Anal. At. Spectrosc.* 8, 1 (1993).
2. T. W. May, R. H. Wiedmeyer, W. G. Brumbaugh, and C. J. Schmitt, *At. Spectrosc.* 8 (5), 133 (1997).
3. Method 200.8, "Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma Mass Spectrometry," in Methods for the Determination of Metals in Environmental Samples, Supplement I, EPA/600/R-94/111, USEPA Monitoring Systems Laboratory, Cincinnati, OH (May 1994).
4. Method 6020, Inductively Coupled Plasma Mass Spectrometry, in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, U.S. Government Printing Office, Springfield, VA (1994).
5. Y. Israel, A. L·sztity, and R. M. Barnes, *Analyst* 114, 1259 (1989).
6. ELAN 6000 Inductively Coupled Plasma Mass Spectrometer Software Guide, 0993-8968 Rev F, Perkin-Elmer SCIEX Instruments, Ontario, Canada (1997).
7. G. Snedecor and W. Cochran, 1967 Statistical Methods, Sixth Edition, The Iowa State University Press, Ames, IA USA, 593 pp.
8. Publication No. 95 101036 00, "Diluter for the Liberty Series," Varian Australia Pty, Ltd. (1991).