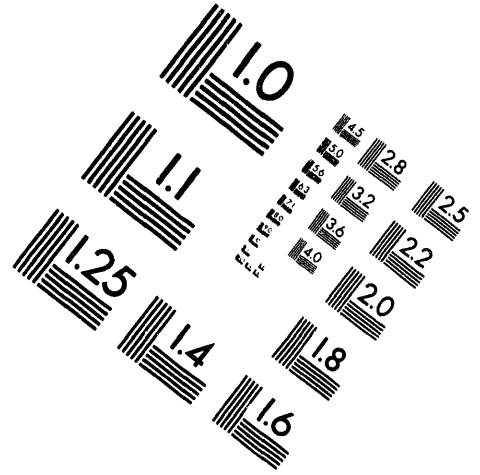
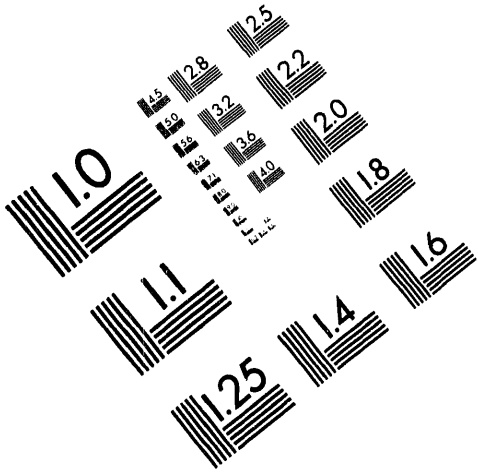




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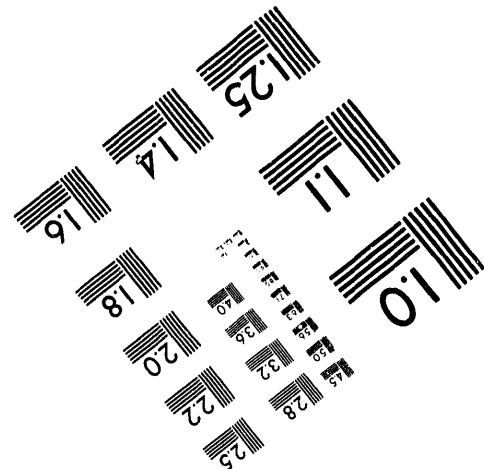
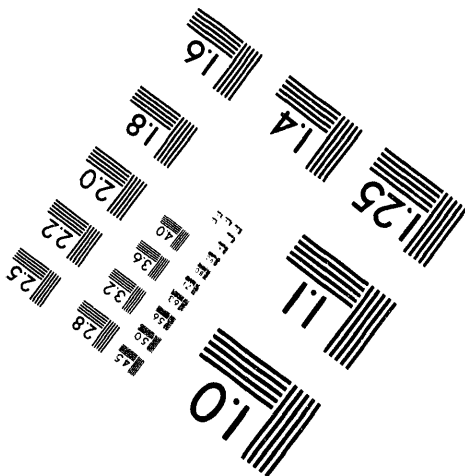
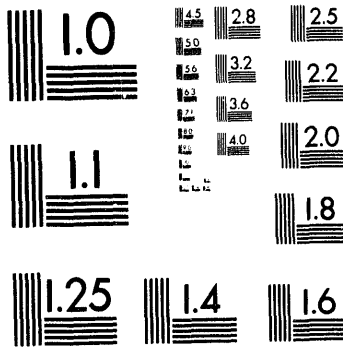
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**THE STABILITY OF CALIBRATION STANDARDS FOR ICP/AES ANALYSIS:
A TWO-YEAR STUDY***

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ABSTRACT

The stability of instrument calibration standards for Inductively Coupled Plasma/Atomic Emission Spectrometric analysis was studied over a two-year period. Data were obtained as functions of analyte concentration, acid type, and acidity. The impact of acid concentration on signal-to-background ratios was also assessed. The results show that, with the appropriate choice of inorganic acid preservatives, most analytes maintain their integrity over extended periods; thus frequent standard preparations are not necessary to obtain valid analytical data. This conclusion allows for more efficient use of commercially purchased reference materials, which should reduce procurement costs and minimize chemical waste.

INTRODUCTION

Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES) is used extensively in the Analytical Chemistry Laboratory (ACL) to characterize diverse analytical samples. This method simultaneously measures the concentrations of multiple cations in solutions. The working standards used for instrument calibration are generally in the 5-20 $\mu\text{g}/\text{mL}$ range. They are prepared from certified single or multi-element stock solutions by serial dilutions and are preserved with inorganic acids. The accuracy and precision of analytical measurements are greatly affected by uncertainties in standard stabilities as functions of preservative type, analyte content, and acid concentration. Consequently, a systematic study was initiated to assess the effect of these parameters on data quality over time. The results have implications regarding standard procurement needs and waste minimization.

EXPERIMENTAL

APPARATUS

The ICP/AES measurements were performed on a spectrometer system that incorporated a 48-channel polychromator and a computer-controlled scanning monochromator (Instruments S. A., Inc., Edison, NJ). Both instruments were focused on a single plasma excitation source. Table 1 lists the instrumentation, and Table 2 details the operating conditions for this two-year study. Typical experimental detection limits (DLs) and their corresponding wavelengths are given in Table 3.

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REAGENTS

Intra-Analyzed HCl and HNO₃ (Baker Chemical Co.) were used in blank and standard preparations. Water for dilutions (≥ 18 Mohm-cm) was obtained from a Sybron/Barnstead ion exchange system. Certified standard stock solutions were purchased from the National Institute of Standards and Technology (NIST), SPEX Industries, and Baker Chemical Co. Test solutions and calibration standards were prepared by making serial dilutions of the concentrates and adjusting to the appropriate acidity. The information on the standard test solutions is summarized in Table 4.

PROCEDURES

The plasma system was optimized with respect to maximum signal-to-background (S/B) ratio as a function of the vertical viewing aperture. The instrument was calibrated at this position by using the two-point calibration procedure with standards and blanks prepared in a 2% acid (HCl or HNO₃) medium. Working standards were prepared on the day of the analytical run and verified against previously used calibration solutions. An agreement of $\pm 3\%$ for this comparative analysis was considered to provide a valid calibration curve for the subsequent analytical run.

Since instrument calibration standards were prepared at a single acid concentration (2%), information on the effect of acidity on signal intensity was needed for data assessment of the diverse analytical matrices. Therefore, S/B ratios were determined as a function of HCl concentration, using a 1- $\mu\text{g/mL}$ multielement standard and a corresponding blank.

The stability of standards is also affected by the possible loss of analyte by diffusion/and or evaporation through plastic containers. Since stock and working standards are stored in polyethylene bottles, diffusion was studied by weight-loss measurements from high density polyethylene (HDPE) and Teflon containers. Bottles were filled with acid solutions, and the change in weight as a function of time was established gravimetrically.

RESULTS AND DISCUSSION

SIGNAL-TO-BACKGROUND RATIOS

One objective of this investigation was to determine the stability of standards as a function of acidity. The analyte response as a function of this parameter is of interest because instrument calibration in our laboratory is generally performed at a 2% acid concentration. Table 5 summarizes S/B ratios for 18 elements in HCl solutions. The data indicate that the presence of mineral acids decreases the emission intensities of atomic and ionic lines for most elements, which is consistent with published results. (1) It has been postulated (cited publication) that these findings are related to the physical state of the plasma at lower acidities ($< 1\text{M}$) and to the reduced rate of sample uptake at higher acid concentrations ($> 1\text{M}$). A few, very sensitive elements (i.e., Be, Ca, Mg, and Sr) exhibit an increase in S/B ratios, an observation inconsistent with the above mechanism. The results show that for best accuracy, calibration standards,

blanks, and samples should be matched with respect to acid concentration. Furthermore, for the purpose of this study, only relative analyte changes should be considered in stability assessments, since instrument calibration was performed at a single acid concentration.

DIFFUSION

Diffusion data for a nine-month period were presented in an earlier report of this study. (2) Continued measurements (>two years) showed these losses to be a function of container type and acid preservative. Solutions in 2% HNO₃ showed the lowest weight loss in HDPE containers (0.5%). Decreases in weight of 0.7% (5% HCl-1% HNO₃) and 0.9% (2% HCl) are considered to be acceptable for the prolonged storage of ICP/AES standards. Solutions prepared in Teflon bottles maintained their weights best in 5% HCl-1% HNO₃ (0.2% loss). Both 2% HCl and 2% HNO₃ showed a diffusion-related decrease of 0.6% and 1.1%, respectively. This controlled study did not address variables pertaining to repeated sampling of bottles and diffusion effects from partially filled containers. The data do, however, suggest that within the accuracy range of ICP/AES (3-10%), changes via these mechanisms would still provide valid analytical data.

STABILITY DATA

Tables 6 and 7 summarize representative stability results in 2% nitric acid.^a The data were obtained from 25 independent measurements over a two-year period. None of the listed analytes, except Sn, show excessive fluctuations at any concentration in this preservative. Similar data sets were obtained with all the other preservatives studied.

As expected, deviations from the mean decrease with increasing analyte content, consistent with more favorable statistics at higher signal intensities. Representative data are shown graphically in Figures 1 and 2. A slight, positive trend in the Cu concentration as a function of time (Figure 1) is apparent; this is probably caused by diffusion losses from progressively smaller sample volumes. Similar behavior was observed for other analytes. The Pb values (Figure 2) remained constant, irrespective of analyte concentration, within the 3-10% stipulated acceptance range.

Standards of Nb and W were studied only in HCl and HCl-HF acids, since HNO₃ is known to cause precipitation. Figure 3 shows the behavior of W as a function of time and acid composition. A similar trend was noted for Nb. These results verify that HF is required to stabilize these elements in calibration standards and ensure longer shelf lives.

At a low analyte concentration (0.2 µg/mL), elements with relatively high DLs (Figure 4) have relative standard deviations (RSDs) exceeding 10%, a result that can be correlated with greater signal fluctuations. For comparison, an analyte with a low DL (more favorable statistics) is shown in Figure 5.

The unexpected, reasonably good stability of Sn in HNO₃ can be explained by the presence of HCl in the stock standard used to prepare the test mixtures. Separate Sn standards prepared in HNO₃ alone deteriorated severely within one week, presumably through the precipitation of

stannic acid. The stability of Ag standards was studied only in HNO₃ and HCl-HNO₃ preservatives, with satisfactory results. The deterioration of Ag solutions can usually be attributed to the introduction of chloride ions during washout procedures.

During the study, it was noted that the Sb and Si results were increasing with time. Closer examination of the stock solutions (2% HCl) used to prepare working standards revealed that precipitates were forming, causing the Si and Sb concentrations in solution to be lower. This resulted in apparently higher values for Si and Sb in the test standards. New stock solutions were used for the working standards in subsequent measurements, and the Sb and Si values for the test matrices returned to an acceptable range. In retrospect, the stability of Si standards should have been examined in the presence of HF, a medium known to promote complexation reactions and thus avoid precipitation due to hydrolysis.

CONCLUSION

The results on the stability of calibration standards for ICP/AES analysis show that a suitable acid preservative enables analyte solutions (5-20 µg/mL) to maintain their integrity over a two-year period. For the wide range of elements studied, a mixture of 5% HCl-1% HNO₃, suggested by the U.S. EPA Contract Laboratory Program (3), appears to provide the best compromise for acceptable shelf lives for most cations. However, for those situations where the relatively high acidities are impractical or undesirable, 2% HCl or 2% HNO₃ stabilizes analytes satisfactorily, provided any chemical incompatibilities (i.e., precipitation, hydrolysis) are resolved.

The variations in S/B ratios as a function of acidity mandate that for best accuracy and precision, calibration standards, blanks, and samples should be matrix-matched (i.e., same acid type and concentration, same major constituents). However, for analytical data normally reported in the accuracy range of 3-10%, approximate acid concentrations are sufficient for satisfactory results.

Changes in analyte concentrations due to evaporation and diffusion through plastic containers did not, over a reasonable time (one year), appear to make a significant contribution to inaccuracies, compared to the more pronounced effects introduced by the excitation and sample transport system. A trend toward increasing concentration was noted over the second year, although the variation was within the expected accuracy range. Partially filled bottles, frequent sampling, and storage conditions could have a considerably larger impact on standard stabilities than those observed here.

This study clearly shows that the frequency of calibration standard preparations could be reduced significantly for ICP/AES analyses at moderate accuracies (3-10%). A complementary investigation at this laboratory on the stability of standards used for graphite furnace atomic absorption (GFAA) analyses concluded that even lower analyte concentrations (≤ 0.25 µg/mL) are stable for at least a nine-month period. (4) Thus, mandated standard preparation requirements for environmental sample analyses could be relaxed, which would result in lower standard procurement costs, waste minimization, and better allocation of analytical effort.

Table 1. Instrumentation

Spectrometers

Polychromator	Instruments S. A. Inc., Model J-Y48P 1-m Paschen-Runge with 2550 grooves/mm holographic concave grating, 20- μ m entrance and 50- μ m exit slits; Hamamatsu R300 and R306 photomultiplier tubes, 48 channels.
Monochromator	Instruments S. A. Inc., Model J-Y38 1-m Czerny-Turner with Spectra-Link controller, 2400 grooves/mm holographic plane grating, variable entrance and exit slits; Hamamatsu R955 photomultiplier tube.

Power and Nebulizer System

Generator	Plasma-Therm Model HFP-2500, 27.12 MHz with 3-turn copper load coil.
Nebulizer Torch	Instruments S. A., Inc. concentric with a Pt-Ir capillary tube. Instruments S. A., Inc. demountable in a Mermet-Trassey configuration.
Spray Chamber	Instruments S. A., Inc. double-barrel, constructed from Ryton.

Computer System

Computer	Digital Equipment Corp. PDP-11/73 with 768K byte of memory, three RL-02 disks.
Terminals	Digital Equipment Corp. DEC Writer III hard copy and DEC VT340 video with graphics.
Software	1. Instruments S. A., Inc.-supplied analytical program run by the DEC RSX-11M operating system. 2. ANL-developed report generation and quality assurance programs.

Table 2. Operating Conditions

Forward R.F. Power	1.10 kW	Argon Flow Rates	
Reflected Power	<5 W	Outer Gas	14 L/min
Observation Height	16mm above load coil	Intermediate Gas	0.4 L/min
		Sheath Gas	0.5 L/min
		Nebulizer Gas	0.6 L/min
Integration Times		Sample Uptake Rate	2.8 mL/min
Polychromator	10 sec		
Monochromator	1 sec		

Table 3. Detection Limits

Element	<u>Wavelength, nm</u>	<u>DL, ^a µg/L</u>
Ag	328.068	1.9
Al	308.215	38.0
As	193.695	52.0
B	208.959	11.0
Ba	233.527	1.3
Be	313.042	0.4
Ca	393.366	1.3
Cd	226.502	3.4
Co	228.616	36.0
Cr	267.716	4.6
Cu	324.754	2.1
Fe	238.204	2.1
Mg	279.553	1.1
Mn	257.610	1.5
Mo	202.030	14.0
Ni	231.604	9.3
Pb	220.353	90.0
Sb	206.833	54.0
Se	196.026	58.0
Si	251.611	14.0
Sn	189.926	30.0
Sr	407.771	0.5
Ti	334.941	2.2
Tl	190.801	24.0
V	292.402	2.9
Zn	213.856	0.5
Zr	343.823	2.7
Monochromator		
Nb	309.418	8.9
W	224.875	7.9

^a Detection Limit (DL) = 3 x the standard deviation of the baseline noise.

Table 4. Summary of Standard Solutions

File Name	Concentration, µg/mL	Elements	Acidity
QF01	0.2	Spex A ^a	1% HNO3 + 0.002% HCl
QF02	0.2	Spex A	2% HNO3 + 0.002% HCl
QF03	0.2	Spex A	5% HNO3 + 0.002% HCl
QF04	0.2	Spex A	1% HCl
QF05	0.2	Spex A	2% HCl
QF06	0.2	Spex A	5% HCl
QF07	0.2	Spex A	5% HCl + 1% HNO3
QF08	1.0	Spex A	1% HNO3 + 0.01% HCl
QF09	1.0	Spex A	2% HNO3 + 0.01% HCl
QF10	1.0	Spex A	5% HNO3 + 0.01% HCl
QF11	1.0	Spex A	1% HCl
QF12	1.0	Spex A	2% HCl
QF13	1.0	Spex A	5% HCl
QF14	1.0	Spex A	5% HCl + 1% HNO3
QF15	4.0	Spex A	1% HNO3 + 0.04% HCl
QF16	4.0	Spex A	2% HNO3 + 0.04% HCl
QF17	4.0	Spex A	5% HNO3 + 0.04% HCl
QF18	4.0	Spex A	1% HCl
QF19	4.0	Spex A	2% HCl
QF20	4.0	Spex A	5% HCl
QF21	4.0	Spex A	5% HCl + 1% HNO3
QF22	10.0	Spex A	2% HNO3 + 0.1% HCl
QF23	10.0	Spex A	2% HCl
QF24	10.0	Spex A	5% HCl + 1% HNO3
QI01	1:10 dil.	ICV-1 ^b	2% HNO3
QI02	1:10 dil.	ICV-1	5% HCl + 1% HNO3
QIC1	1:10 dil.	ICV-1	2% HNO3
QIC2	1:10 dil.	ICV-1	5% HCl + 1% HNO3
QA01	0.2	Ag	1% HNO3
QA02	0.2	Ag	2% HNO3
QA03	0.2	Ag	5% HNO3
QA04	1.0	Ag	1% HNO3
QA05	1.0	Ag	2% HNO3
QA06	1.0	Ag	5% HNO3
QA07	4.0	Ag	1% HNO3
QA08	4.0	Ag	2% HNO3
QA09	4.0	Ag	5% HNO3
QA10	10.0	Ag	2% HNO3

^a Spex A: Al,Ba,Be,Ca,Cd,Co,Cr,Cu,Fe,Mg,Mn,Ni,Pb,Sn,Sr,V,Zn,Zr

^b ICV-1: Ag,Al,Ba,Be,Ca,Cd,Co,Cr,Cu,Fe,Mg,Mn,Ni,Pb,V,Zn

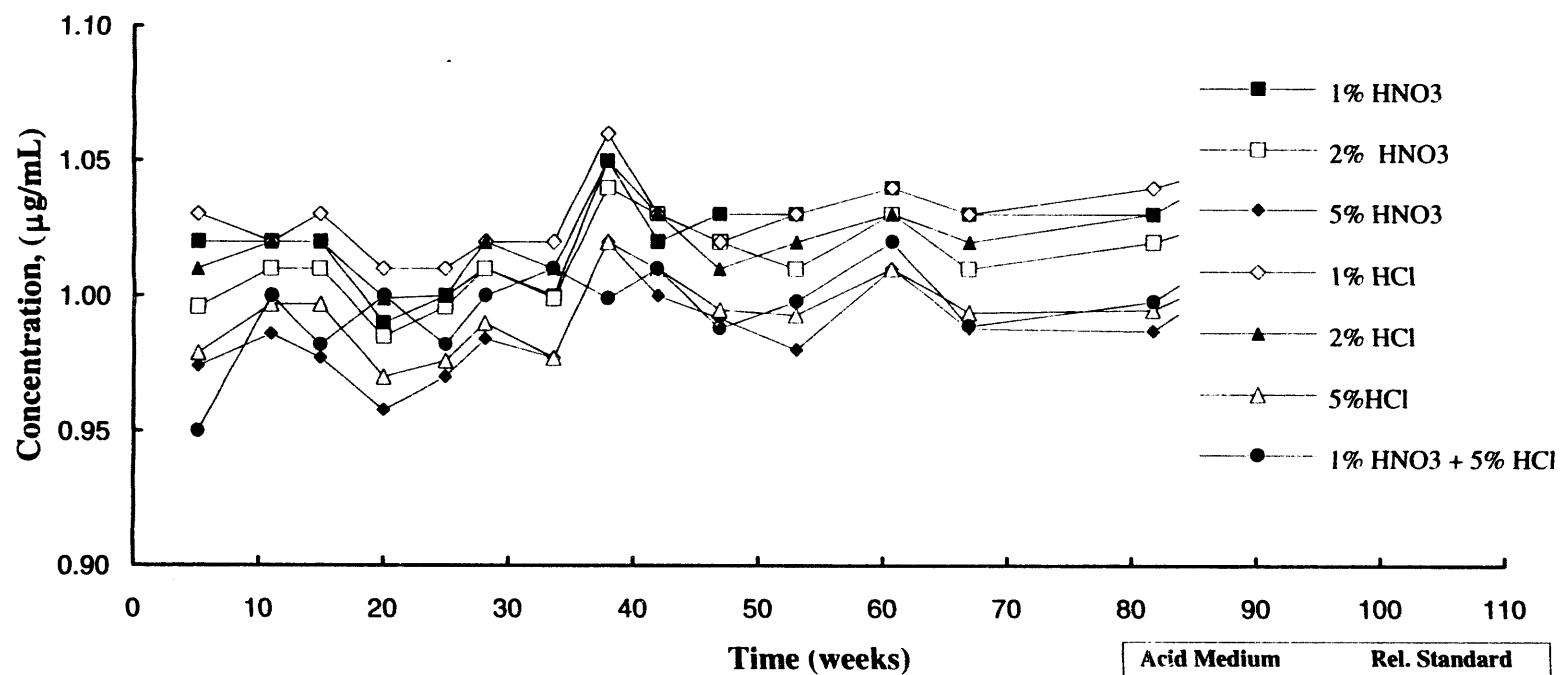
Table 4. Summary of Standard Solutions (cont'd)

File Name	Concentration, mg/mL	Elements	Acidity
QSi1	0.5; 1.0	B, Mo, Ti; Si	2% HNO3
QSi2	0.5; 1.0	B, Mo, Ti; Si	2% HCl
QSi3	0.5; 1.0	B, Mo, Ti; Si	5% HCl + 1% HNO3
QSi4	2.5; 5.0	B, Mo, Ti; Si	2% HNO3
QSi5	2.5; 5.0	B, Mo, Ti; Si	2% HCl
QSi6	2.5; 5.0	B, Mo, Ti; Si	5% HCl + 1% HNO3
QSi7	10.0; 20.0	B, Mo, Ti; Si	2% HNO3
QSi8	10.0; 20.0	B, Mo, Ti; Si	2% HCl
QSi9	10.0; 20.0	B, Mo, Ti; Si	5% HCl + 1% HNO3
QAs1	5.0	As, Sb, Se	2% HNO3
QAs2	5.0	As, Sb, Se	2% HCl
QAs3	5.0	As, Sb, Se	5% HCl + 1% HNO3
QAs4	20.0	As, Sb, Se	2% HNO3
QAs5	20.0	As, Sb, Se	2% HCl
QAs6	20.0	As, Sb, Se	5% HCl + 1% HNO3
QSn1	5.0	Sn	2% HNO3
QSn2	5.0	Sn	2% HCl
QSn3	5.0	Sn	5% HCl + 1% HNO3
QSn4	20.0	Sn	2% HNO3
QSn5	20.0	Sn	2% HCl
QSn6	20.0	Sn	5% HCl + 1% HNO3
QW01	1.0	W	2% HCl
QW02	1.0	W	2% HCl + 0.5% HF
QW03	5.0	W	2% HCl
QW04	5.0	W	2% HCl + 0.5% HF
QW05	20.0	W	2% HCl
QW06	20.0	W	2% HCl + 0.5% HF
QNb1	1.0	Nb	2% HCl
QNb2	1.0	Nb	2% HCl + 0.5% HF
QNb3	5.0	Nb	2% HCl
QNb4	5.0	Nb	2% HCl + 0.5% HF
QNb5	20.0	Nb	2% HCl
QNb6	20.0	Nb	2% HCl + 0.5% HF

Table 5. Signal-to-Background Ratio vs. Acidity

Element	<u>Signal-to-Background Ratio</u>					<u>% Change</u>	
	1% HCl	2% HCl	5% HCl	10% HCl	20% HCl	1-5% HCl	1-20% HCl
Al	1.63	1.64	1.70	1.60	1.60	+4.3	-1.8
Ba	6.50	6.44	6.35	6.20	6.04	-2.3	-7.1
Be	83.4	84.5	88.4	90.7	91.2	+6.0	+9.3
Ca	14.58	15.47	19.13	18.86	18.08	+31.2	+24.0
Cd	7.75	7.65	7.60	7.43	7.26	-1.9	-6.3
Co	2.99	2.98	2.96	2.94	2.84	-1.0	-3.4
Cr	4.36	4.30	4.28	4.25	4.14	-1.8	-5.0
Cu	5.38	5.29	5.31	5.23	5.22	-1.3	-3.0
Fe	5.02	4.86	4.80	4.69	4.62	-4.4	-8.0
Mg	30.1	29.9	38.7	41.2	38.4	+28.6	+27.6
Mn	17.75	17.57	17.45	17.05	16.64	-1.7	-6.3
Ni	2.69	2.71	2.70	2.65	2.59	-0.4	-3.7
Pb	1.57	1.54	1.56	1.53	1.51	-0.6	-3.8
Sn	1.68	1.65	1.61	1.67	1.60	-4.2	-4.8
Sr	63.8	64.8	68.9	70.3	71.2	+8.0	+11.6
V	4.23	4.21	4.19	4.12	4.03	-0.9	-4.7
Zn	18.97	18.90	19.17	18.33	17.43	+1.0	-8.1
Zr	4.21	4.21	4.26	4.19	4.14	+1.1	-1.7

Figure 1. Copper Concentration as a Function of Time



Acid Medium	Rel. Standard Deviation
1% HNO3	1.80
2% HNO3	2.28
5% HNO3	1.75
1% HCl	1.85
2% HCl	1.96
5% HCl	1.90
1% HNO3 + 5% HCl	1.73

Figure 2. Concentration of Lead in 2% HCl as a Function of Time

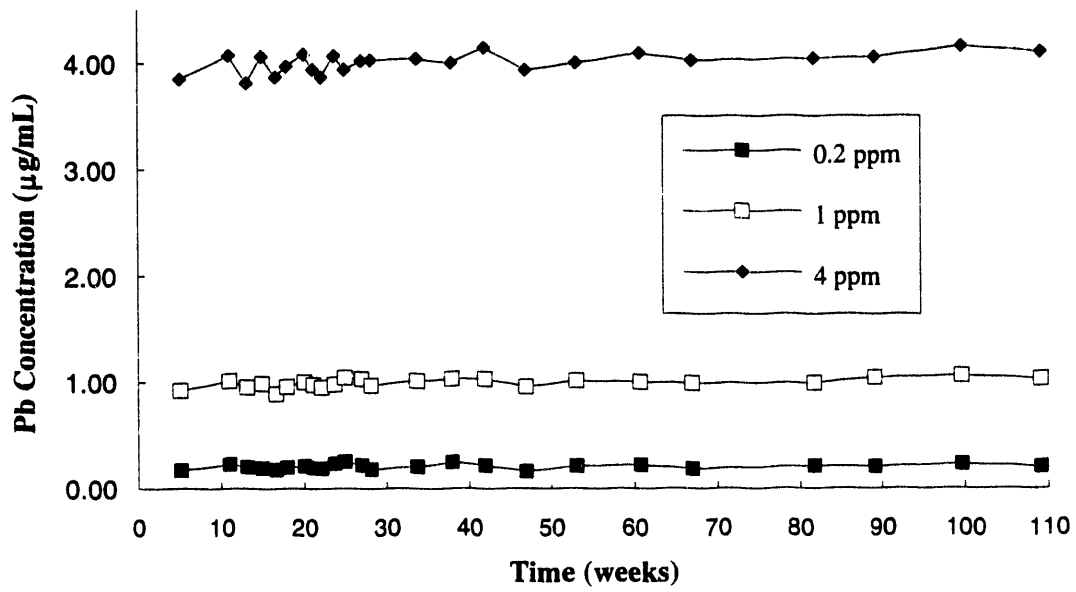


Figure 3. Tungsten Concentration as a Function of Time

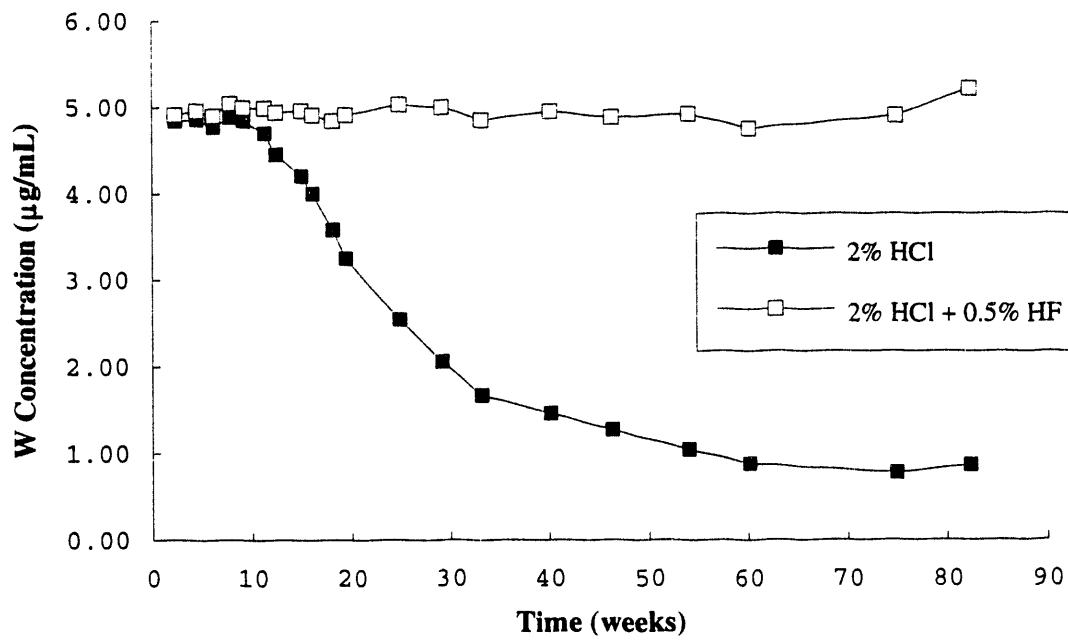


Table 6. Stability of Spex A Standard in 2% Nitric Acid over a Two-Year Period

Element	Concentration 0.200 µg/mL		1.00 µg/mL		4.00 µg/mL		10.00 µg/mL	
	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Ag	0.200	0.010	1.026	0.017	4.018	0.051	9.800	0.346
Al	0.206	0.020	1.007	0.042	4.051	0.073	10.24	0.236
Ba	0.203	0.004	0.998	0.024	4.018	0.066	10.06	0.274
Be	0.200	0.003	0.973	0.021	3.970	0.065	9.990	0.231
Ca	0.180	0.028	1.000	0.035	4.064	0.092	10.39	0.274
Cd	0.204	0.003	0.999	0.021	3.989	0.073	10.11	0.234
Co	0.207	0.006	1.013	0.027	4.016	0.072	10.26	0.240
Cr	0.212	0.009	1.033	0.042	4.134	0.135	10.39	0.439
Cu	0.206	0.004	1.009	0.023	4.010	0.066	10.25	0.201
Fe	0.203	0.010	1.006	0.026	4.059	0.074	10.17	0.274
Mg	0.201	0.004	1.005	0.019	4.045	0.068	10.22	0.214
Mn	0.206	0.003	1.005	0.020	4.022	0.074	10.20	0.230
Ni	0.203	0.008	0.999	0.026	4.012	0.072	9.946	0.236
Pb	0.196	0.030	0.992	0.049	4.014	0.075	9.949	0.232
Sn	0.223	0.097	0.994	0.255	3.623	0.777	8.432	0.649
Sr	0.204	0.004	0.992	0.024	4.046	0.082	10.25	0.294
V	0.210	0.005	1.016	0.021	4.018	0.064	10.26	0.217
Zn	0.204	0.005	0.990	0.029	4.026	0.102	10.14	0.303
Zr	0.200	0.005	0.996	0.017	3.948	0.088	10.14	0.160

Table 7. Stability of Selected Elements in 2% Nitric Acid over a Two-Year Period

Concentration	0.500 µg/mL		2.50 µg/mL		10.0 µg/mL	
Element	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
B	0.496	0.018	2.418	0.070	9.855	0.207
Mo	0.496	0.024	2.439	0.071	10.06	0.20
Ti	0.511	0.010	2.517	0.070	10.25	0.26

Concentration	1.00 µg/mL		5.00 µg/mL		20.0 µg/mL	
Si	1.023	0.058	5.057	0.217	20.95	0.66
As			5.201	0.148	20.75	0.48
Sb			5.344	0.360	21.26	1.43
Se			4.906	0.141	20.2i	0.37

Figure 4. Relative Standard Deviation for Aluminum as a Function of Concentration

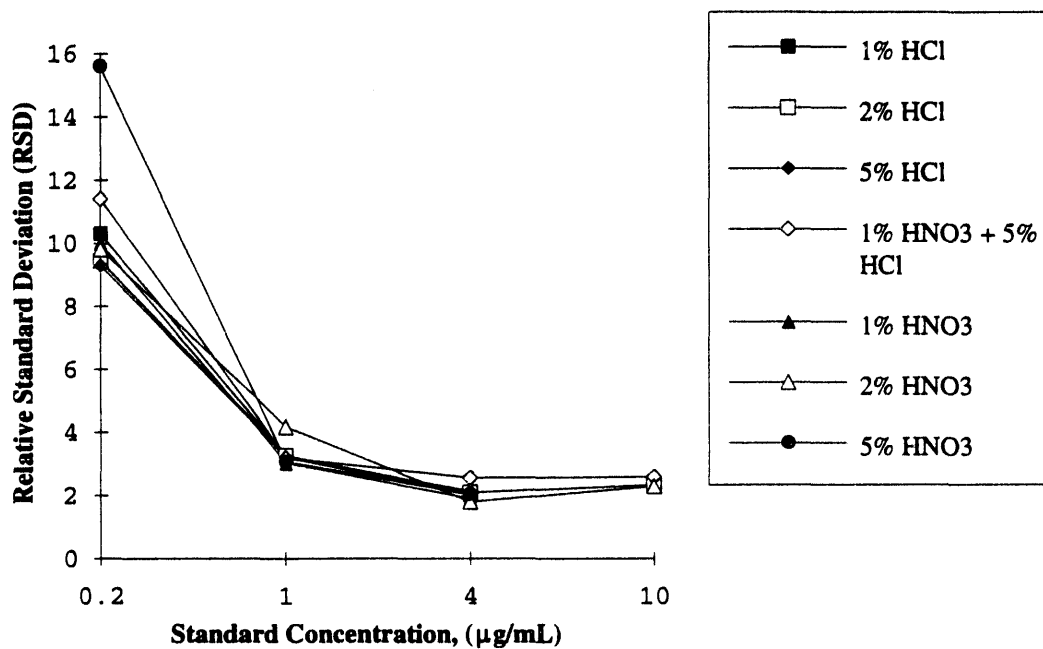
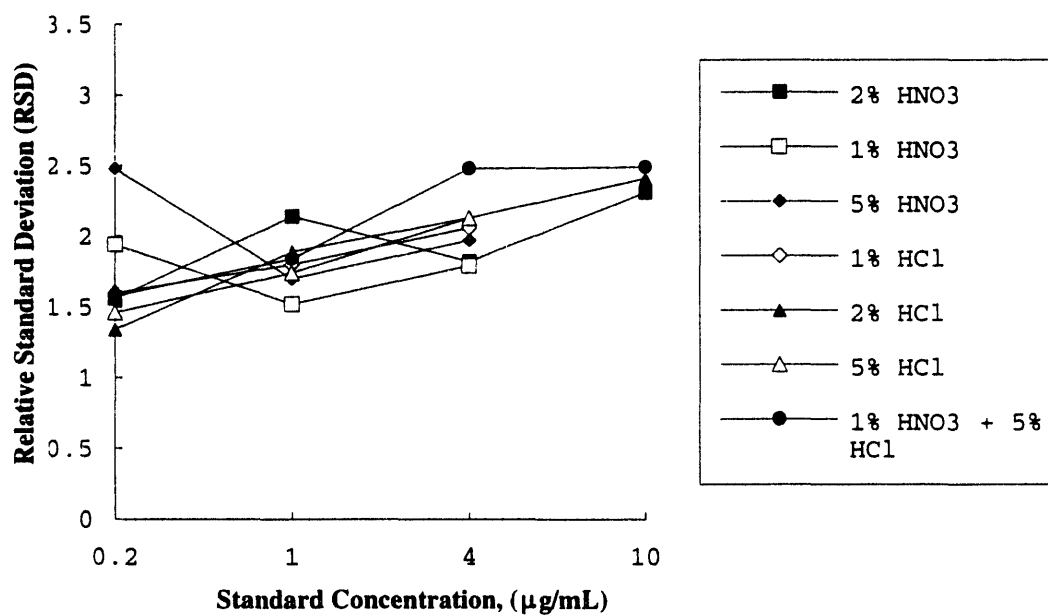


Figure 5. Relative Standard Deviation for Cadmium as a Function Of Concentration



^aThe entire data base could not be included in this presentation due to space limitations. This information is available from the authors upon request.

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