ANALYSIS OF BARIUM IN SEDIMENTS

by

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INTRODUCTION

The use of the d.c. (direct current) argon plasma as an excitation source in spectrochemical analysis has permitted high analytical sensitivity for barium while achieving reproducibility close to levels typical for flame (emission or absorption) analysis. Detection limits for Ba in the d.c. plasma have been lowered to approximately 1 ppm (Reednick, 1979) in solids, whereas the detection limits for Ba using X-ray fluorescence is 45 ppm, (J. Commeau, U.S. Geological Survey, oral communication, 1979), that of atomic absorption is 10 ppm (Winefordner, 1976), and that of neutron activation analysis is 10 ppm (Ward, 1978). However, variations in emission intensity have been attributed to matrix effects including effects caused by refractory-component formers in the arc, the amount of solids introduced, background emission levels, the portion of plasma selected for imaging on the photodetector, and spectral interferences (Bankston and Fisher, 1977; Skogerboe and Urasa, 1978; Johnson and others, 1979). Geological matrices may range from nearly pure SiO_2 and $CaCO_3$ to aluminosilicates, and all combinations of these end members exist. Significant concentrations of other constituents may also occur in mineral lattices. The principal objective of this work has been to devise an analytical procedure that could be insensitive to wide shifts in geological matrix, as well as to varying forms of Ba, e.g., silicate, carbonate, or sulfate binding. The principal analyst in this study has been P.C. Bowker. Comments and criticism on this report have been provided by D.C. Bankston, M.H. Bothner, and E. Winget.

EXPERIMENTAL PROCEDURE

Instruments Used

A Spectraspan IIB echelle-grating emission spectrometer with a three-electrode d.c. argon plasma excitation source (Spectrametrics, Inc.[1]) was used to carry out all analyses. General characteristics of d.c. plasma sources and the specifics of the echelle-grating spectrometer used in this study have been described previously (Fairless, 1978; Reednick, 1979; Zander and Keliher, 1979). The sample is introduced into the system as a liquid, which is pumped to a venturi-type aspirator and into a spray chamber. Aerosol is carried with a stream of argon and is delivered from below to the inverted Y plasma arc. Zero velocity, the state of maximum analytical usefulness (Fairless, 1978), is reached by the aerosol particles just before they enter the plasma. For most elements, the spectrometer-excitation system produces a linear output for more than three orders of magnitude in concentrations, giving it flexibility suitable to a variety of sample types and analyte concentrations.

A peristaltic pump is used for liquid delivery in our system. To facilitate the introduction of buffers and avoid the task of adding them to each individual sample and standard, a two-channel pumping system was utilized. The system is like that introduced by Jenne (Ball and others, 1978); two tubes are led through the pump and are connected by a "T" between the pump and nebulizer. In this fashion, the buffer and sample or standard are pumped separately to the "T" connection and then are mixed in-line and in the spray chamber before delivery to the plasma. Further utilization of the two-channel system is explained below under "in line additions".

Sample Preparation

In this study sediments were dissolved by fusion with lithium borate flux according to methods described by Suhr and Ingamells (1966) and Ingamells (1970). A 100-mg sample was ground to pass a 200-mesh nylon screen, mixed 1-to-7 with flux, transferred to a graphite cruicible, and fused at 950°C in a muffle furnace for 15 minutes. The resulting molten glass was poured into a 100-ml teflon beaker containing 3% nitric acid, was stirred until the fusion had dissolved (about 1/2 hour), and then was diluted to 200 ml.

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[1] Use of trade names in this publication is for identification only and does not constitute endorsement by the U.S. Geological Survey.

Solution Preparation

Fused standard

A. Five-tenths gram $BaSO_4$ was mixed with 4.5 gms SiO_2 (both Johnson-Matthey Spec-Pure Powders) in Spex Mixer Mill.

B. One-tenth gram of material mixed in step A was mixed with 0.7 gm of "Spectroflux" (commercial mixture of lithium metaborate and tetraborate), was fused at 950°C, and then was dissolved and diluted to 200 ml with 3% HNO_3.

C. The solution made in step B was used as a stock standard to make up a range of working standards (30-3,000 ppb Ba) by diluting with background fused SiO_2 blank solution.

Fused SiO_2 ("blank")

Eight-tenths gram of a 1 + 7 SiO_2 Spectroflux mixture was fused, dissolved, and diluted to 100 ml with 3% HNO_3. This was a double-strength solution used to dilute standards. Twenty such fusions were made to provide 2 liters of solution.

Nonfused standard

Nonfused stock barium standards made from soluble salt were diluted to the same range as fused 10% working standard (30-3,000 ppb) with the fused SiO_2 blank solution. This set of standards is referred to as "Si".

Standards containing nonfused Ba in a matrix of Ca and Al (Ca, Al, All) and fused SiO_2 solution

Five hundred ppm of Ca and Al were each added to a series of nonfused standards of Ba (30, 300, and 3,000 ppb), and 1 ml of 5% solution of Ca and Al/100 ml was added to a third series of nonfused standards of Ba. All three series contain fused SiO_2 solution. The third series containing Al, Ca, and fused SiO_2 solution is designated "All" in this report. Ca was prepared by dissolving $CaCO_3$ in acid, and the Al solution was a commercial standard.

Aqueous standards (Aq)

Stock standards having a range of Ba concentrations were diluted with 3% HNO_3 only. No background or elemental matrix additions were made. These are referred to as "Aq" and were used in this experiment as reference for the enhancement behavior of various added components.

Table 1 shows the concentration of the various components found in the above-described solutions.

Buffers

Buffering element solutions of 0.05%, 0.1%, 0.2%, 0.5%, 1%, and 2% concentration were made up with a final acid concentration of 3% HNO_3 as follows:

Buffer element	Compound	Dissolution
Li	Li_2CO_3	reacted with NHO_3
Cs	CsCl	H_2O
K	KCl	H_2O
La	La_2O_3	reacted with HNO_3
Na	NaCl	H_2O

RESULTS

Tests for interelement and matrix effects

The first series on standards of Ba with and without matrix additions is depicted in figure 1. As previous studies have shown (Skogerboe and Urasa, 1978), alkali (lithium in fluxing material) exerts an enhancing effect on emission intensities (compare "fused std" with "Aq" in fig. 1).

In this study, ionization buffers of potassium, lithium, cesium, and sodium ranging from 500 to 20,000 ppm were tested. Potassium buffer at the 2% level showed a corrective effect, but erratic variations in signal as great as 10% were observed, as well as a rapid drop in sensitivity during the run. The same effect was noted for cesium and lithium at this level and is assumed to be due to clogging by salt in the delivery system. Sodium did not show instability in emission but would not correct for the enhancement by calcium.

As alkali buffering alone did not compensate for matrix variations, lanthanum was added to buffer the system with respect to possible volatilization behavior. Aluminum in particular has been stated to form refractory compounds such as aluminates with alkali earths (Skogerboe and Urasa, 1978) (see discussion below). Lanthanum concentrations of 500 to 20,000 ppm were incorporated in a series of solutions containing constant analyte at various concentrations. La at 1% concentration in the presence of lithium borate at a 3,500-ppm level was found to remove the effect of variable matrix to within 2% (fig. 2). A residual difference between aqueous standards and Li-containing solutions shows that alkali buffering is an essential component in elimination of matrix effects. Table 2 shows the close fit of line slopes in the presence of lathanum and an overall reduction in intensity. Increasing La alone to 2% reduced deviation between "aqueous" and fused standards but did not eliminate it (fig. 3).

Table 1. Concentrations of working solutions described in the text. [Matrix components of SiO_2, Li borate, and HNO_3 were made constant by adding one-half volume of a double strength SiO_2-Li borate solution and appropriate volume of HNO_3 before each working solution was volumetrically fixed. Buffer solutions made from Li_2CO_3, CsCl, KCl, La_2O_3, and NaCl in concentrations of 0.05%, 0.1%, 0.2%, 0.5%, 1%, and 2% in 3% HNO_3.]

Solution	Ba	SiO_2	Li borate	%HNO_3	Ca	Al
Fused std.	0.3-3	500-550*	3,500-3,850*	3	-	-
"blank"	-	500	3,500	3	-	-
"nonfused std."	.03-3	500	3,500	3	-	-
"Ca"	.03-3	500	3,500	3	500	-
"Al"	.03-3	500	3,500	3	-	500
"All"	.03-3	500	3,500	3	500	500
Aqueous stds.	.03-3	-	-	3	-	-

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*Range of components is due to dilution of different volumes of an already fused standard solution.

Figure 1. Effect of variable matrix on barium emission.

<u>Aq</u> refers to Ba in 3% nitric acid.

<u>Nonfused</u> <u>std</u>. refers to nonfused standards made with fused SiO_2 solution containing lithium borate.

<u>Fused</u> <u>std</u>. refers to fused standard diluted with fused SiO_2 solution.

<u>Al</u> and <u>Ca</u> refer to nonfused standards diluted with fused SiO_2 solution plus 500 ppm Al or Ca.

<u>All</u>, nonfused standard diluted with fused SiO_2 solution plus both Al and Ca additions.

See table 1 for actual concentrations of solutes other than analyte.

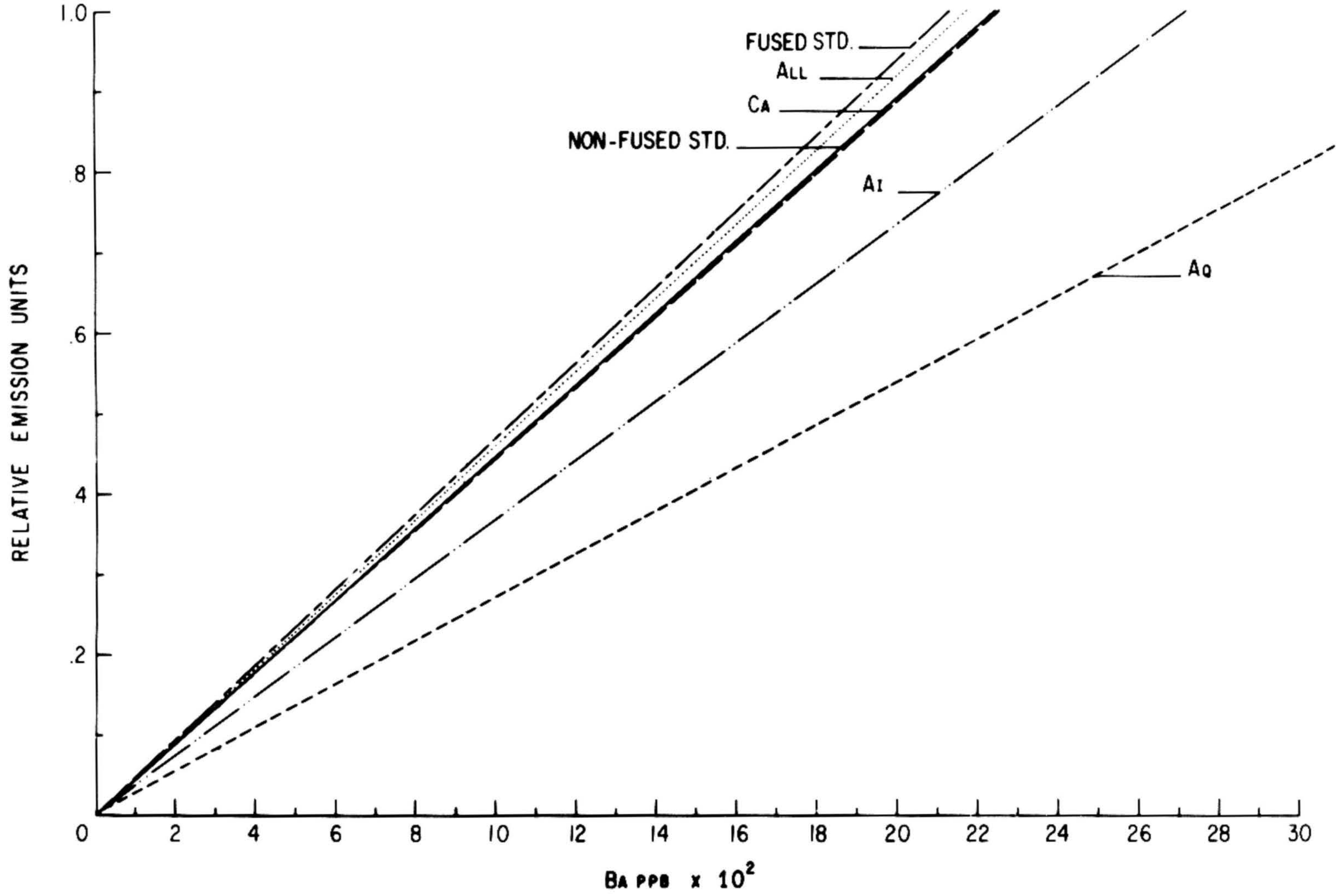

Figure 1. Effect of variable matrix on barium emission.

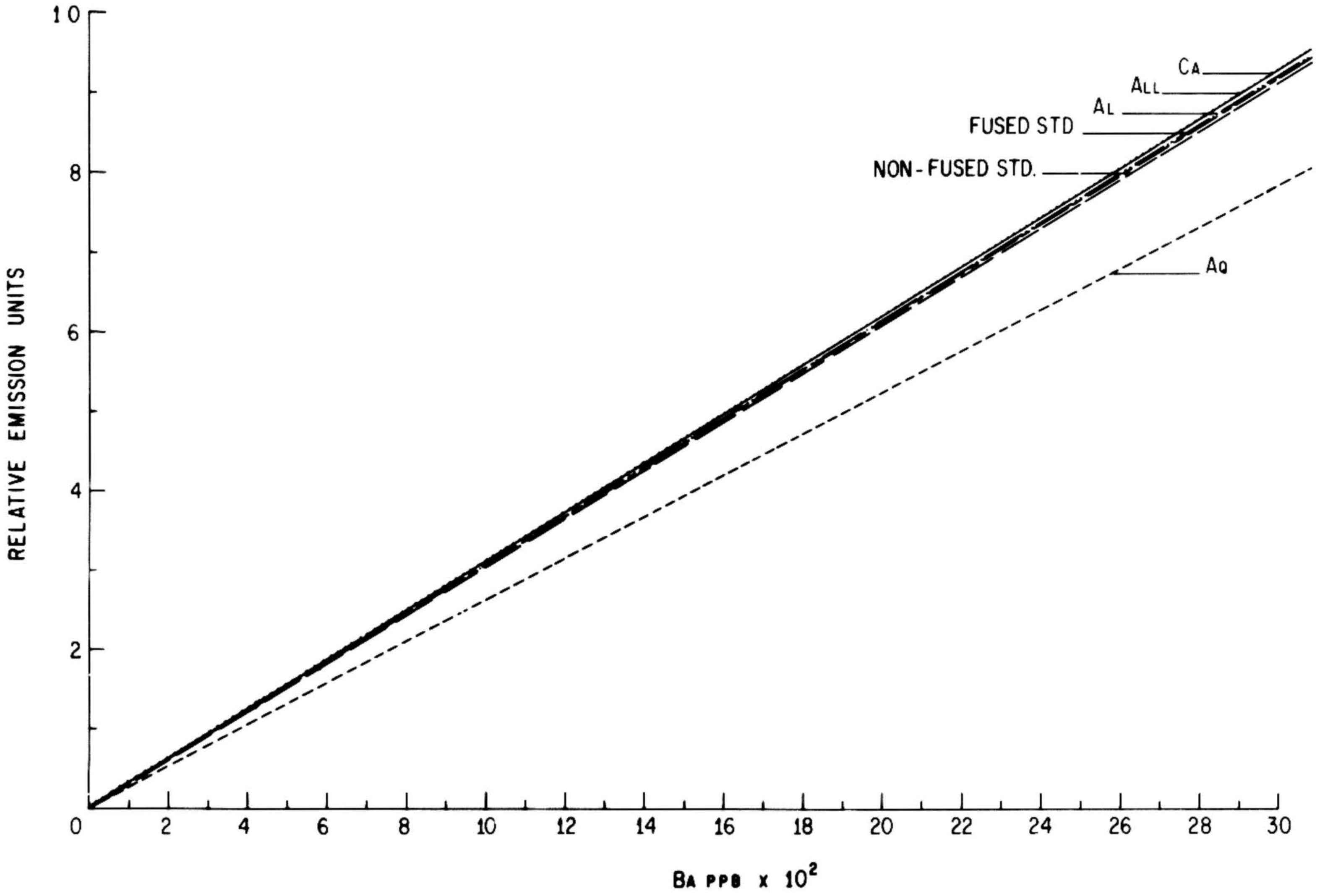

Figure 2. Effect of variable matrix on barium emission when 1% La buffer is added. See caption of figure 1 for explanation of terms.

Table 2. Slopes and y intercepts of standard curves of solutions (figs. 1,2) run with and without 1% La.

Line	Ba No La	Ba 1% La
Aq.	0.534X + .08	0.522X + .04
Al	0.736X + .02	0.616X - .02
nonfused	0.882X + .06	0.612X + .01
Ca	0.886X + .04	0.622X + .05
All	0.916X + .04	0.622X + .03
fused	0.944X - .05	0.614X + .02

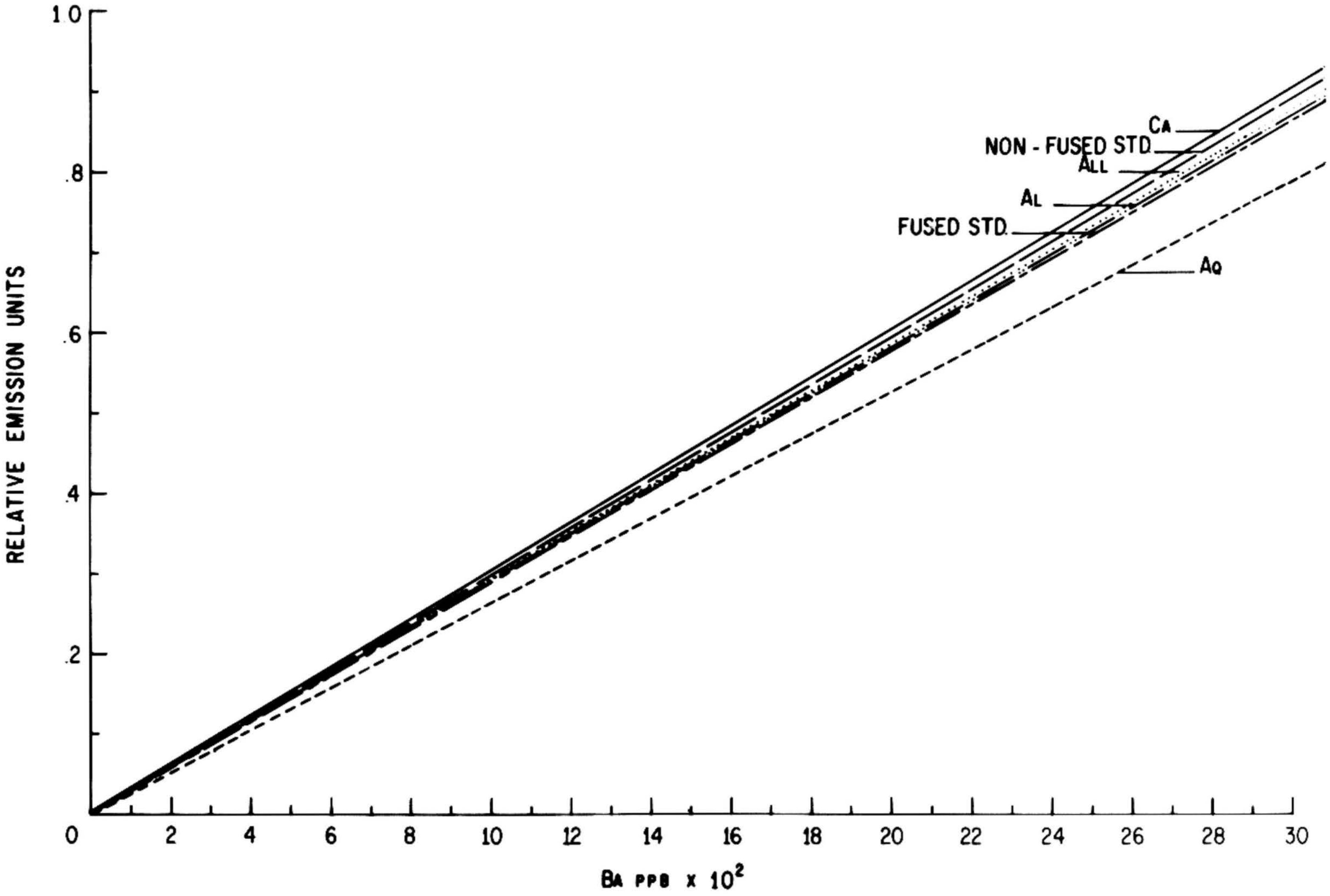

Figure 3. Effect of variable matrix on barium emission when 2% La buffer is added. See caption of figure 1 for explanation of terms.

The results shown in figure 2 also provide a check on the fusion step, inasmuch as the addition of 1% La also yields signal unity for standards prepared by direct dilution and for those carried through a fusion procedure. The figures used in this paper are for graphic demonstration of matrix effects only. They do not contain actual data points, which would show analytical scatter because clutter and overlap would result, especially when slope unity is approached. Instead, relative standard deviations (RSD) of several runs of Ba are given in table 3. These were established by using the regression curve of the run and calculating apparent concentrations of a given standard from each reading of the standard's "data set". "Data set" refers to five or six 10-second integrated readouts, which are usually used to acquire a mean relative intensity value for the standard. At least two "data sets" were used to calculate any RSD. A limiting factor for this technique is instrument drift. Normally, drift is corrected by using ratios consisting of average readings divided by the apparent reading of a check standard periodically throughout the run.

In-line additions

The use of standard additions is an accepted means of analysis to minimize matrix problems. To shorten the time involved in splitting samples and adding standards, we added in-line spikes through a two-channel pumping system. To check the reliability and equality of flow in the two limbs of the system constructed from Autoanalyzer components, solutions of aqueous standards pumped through both tubes were compared with introduction of a stock solution having twice the concentration of analyte in one tube and blank through the other. Even with matrix differences, the two methods of introduction produced acceptable signal duplication (fig. 4). This method has the further advantage of allowing the simultaneous introduction of otherwise incompatible solutions (e.g., those that would precipitate on standing).

DISCUSSION

Skogerboe and Urasa (1978) and Taylor (in press) recently discussed the long-known depressant effect of aluminum and phosphorus on calcium emission. The assumption that formation of less volatile (refractory) components was responsible for depression of Ca emission was documented by these authors by selectively measuring calcium emission in various parts of the plasma. Suppression effects could be eliminated for large excesses of phosphorous or aluminum by measuring emission in a region 6 mm above the zone of maximum excitation (Skogerboe and Urasa, 1978). These authors also showed that although the suppressant effect of Al or Ca can be reduced or eliminated by arc positioning, a twelve-fold loss in overall analytical sensitivity results; i.e., the "hotter" zone permits lower selective excitation of resonance lines of the alkali earth elements. Although this loss of sensitivity was regarded as tolerable for calcium (major-element) analysis, it is undesirable for our trace-element studies. Our work confirms suppressant effects of Al upon Ba as well as the reduction of suppression by arc positioning and its accompanying loss of overall analytical sensitivity.

Table 3. Relative standard deviations (RSD) of apparent concentrations of given standards derived from "data sets" (defined in text) of the standard. Readout components of sets are not corrected for drift.

	"Data sets"	Readings	Conc. level (μg/l)	RSD (%)
Run #1	7	35	3,000	2.05
	2	11	20	4.14
	2	10	200	.88
	2	10	2,000	1.42
	3	15	3,000	.58
Run #2	3	15	3,000	.61
Run #3	4	21	3,000	5.77*
	2	10	3,000	1.78
Run #4	3	15	3,000	1.58
	2	10	3,000	2.12
Run #5	3	15	3,000	1.65

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*Data biased by a radical signal shift within the data set.

Figure 4. Comparison of in-line spikes and single-solution standards. Single solutions refer to aqueous barium standards to which 500 mg/l of Ca, Si, or Al has been added. Aq refers to Ba in 3% nitric acid. Solutions were pumped through both introduction tubes of the dual pumping system. In-line spikes were made by pumping a solution containing twice the concentration of background through one tube and twice the concentration of Ba through the other. Mixing resulted in solutions having concentration equal to those of single solutions. Solid circles refer to single solution; hollow circles refer to dual solutions.

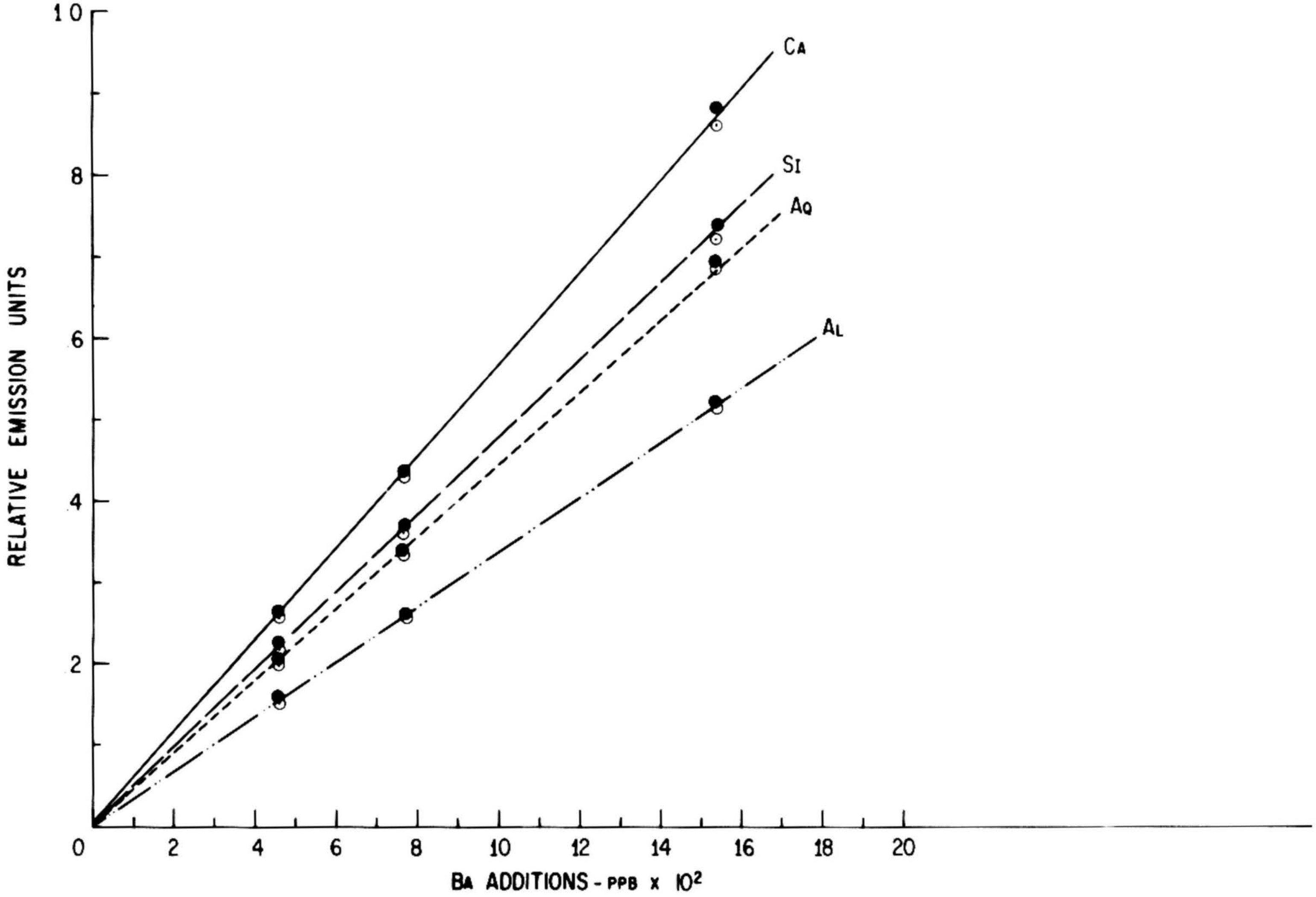

Figure 4. Comparison of in-line spikes and single-solution standards.

Table 4. Comparison of mean barium concentrations determined by different methods for standard rock samples (ppm). [SD refers to standard deviation where available. Data followed by an asterisk are means and standard deviations of values from different laboratories (AGV-1 and BCR-1). Other data are from single laboratories and standard deviations are for replicate analyses. All literature data are from authors cited in Flanagan (1976). For further explanation, see text.]

Sample[1]	INAA[2]	SD	XRF[2]	SD	Quant. sp.[2]	SD	Isotope dil.[2]	SD	Best values	Plasma	SD
ACV-1	1,110*	90	1,211*	101	1,267*	194	1,208	-	1,208	1,228	47
MAG-1	311	78	513	8	493	70	476	2.6	-	512	20
SGR-1	225	120	328	8	322	12	286	3.6	-	312	13
BCR-1	722*	118	659*	86	740*	63	676*	20	675	700	33

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[1] ACV-1 is an andesite from Oregon; MAG-1 is a clayey marine mud from the Gulf of Maine; SGR-1 is shale of the Green River Formation, Utah; BCR-1 is a basalt from the Columbia River Basalt Group, Washington-Oregon.

[2] INAA refers to instrumental neutron-activation analysis; XRF is X-ray fluorescence; Quant. sp. is quantitative optical emission spectroscopy: and Isotope dil. refers to isotope-dilution (mass spectrometric) analysis.

Uncertainty remains regarding the precise processes and chemical species involved in the "volatility effect". For example, temperatures varying from 2,500 K to 5,000 K were calculated by various means for the zone of maximum (emission) excitation in the d.c. plasma (Skogerboe and others, 1976). The lower temperature might permit suppression due to formation of refractory components, whereas the higher temperature should dissociate all known chemical components.

We have chosen to add La in the presence of alkali buffer as an empirically confirmed effective releasing agent. This approach to suppression of "volatility" effects is preferred to arc positioning because it is insensitive both to minor changes in optical configuration and to extreme matrix changes, and does not sacrifice analytical sensitivity.

To date, each of the plasma-emission excitation devices has shown specific advantages and disadvantages (Greenfield and others, 1964; Sutton and others, 1978; Burman and Bostrom, 1979). The inductively coupled plasma (ICP) appears to be less subject to matrix effects than the d.c. plasma or the microwave plasma excitation systems. However, currently available ICP instrumentation is limited by the total salt concentration that can be aspirated in solutions, which, in turn, limits both the analytical sensitivity necessary for determination of constituents in solid materials and the concentration of spectrochemical buffers that may be added (Burman and Bostrom, 1979).

Rock standards

Table 4 provides a comparison between present data and published barium analyses on four standard samples having abundant interlaboratory analytical control. The isotope dilution data are the most precise and consistently accurate, whereas the neutron activation data have the highest standard deviations. The quality of the isotope dilution values is not surprising because the technique is inherently relatively free from systematic error if properly executed and is typically used by highly experienced analysts. In addition, 40 or more scans on a mass spectrometer are averaged to obtain one value, thereby enhancing precision of data. "Best" values chosen by Flanagan (1976) have apparently been selected from isotope-dilution data for the older standards (AGV-1 and BCR-1).

The plasma arc data reported here are within analytical standard deviation of "best" values recorded by Flanagan (1976). We, therefore, conclude that our studies suggesting freedom from matrix effect are borne out by the comparisons with standard rocks.

Sediment samples

Two sets of marine sediment samples collected for the U.S. Bureau of Land Management (BLM) were sent to our laboratory for barium analysis. One set, collected by the Continental Shelf Associates, Inc. (CSA), off Key West, was received in finely ground homogenized form. The other set, MAFLA

(Mississippi-Alabama-Florida Shelf) samples from Ter Eco Corp., arrived in natural state except for being freeze-dried upon arrival at the laboratory; this gave us an opportunity to see whether variations in barium content existed in splits of unhomogenized samples. Table 5 gives a visual description of the MAFLA samples to demonstrate the unhomogenized nature of these sediments. Each sample was shaken with a ball pestle in a mixer mill just long enough to reduce the grain size to fit through the slots of a mechanical splitter. After splitting, each portion was ground, meshed, and homogenized. Two aliquots of split #1 were taken, and only one aliquot of split #2 was used for comparison. Expecting some rather significant differences between splits, we were surprised to find the concentration from one split to the next was well within the analytical standard deviation between aliquots of one split. Therefore, the results found in table 6 for the MAFLA samples are actually the mean of both splits of one sample, and the results for the CSA samples are the mean of two aliquots of one sample.

The data in table 6 indicate barium concentrations on the order of concentrations previously found typical of reef carbonates and oolitic (carbonate) muds. Stehli and Hower (1961), for example, found a range from 10 to 61 ppm Ba in 59 samples containing an average of 18.4 ppm Ba. These are among the lowest barium concentrations of all sediments. Clayey sediments, for example, have Ba contents ranging from a few hundred parts per million to more than 1,000 ppm, and deep-sea sediments have still larger concentrations.

CONCLUSIONS

We have found that the d.c. plasma arc is suited to analysis of barium in a wide range of sedimentary rock samples. Analytical ranges from 10 to more than 3,000 ppm Ba in rock were studied in this work. Lower values may be determined by decreasing dilution of the lithium borate fusion with 3% HNO_3.

Both alkali (3,500 ppm lithium borate) and lanthanum salts (1%) in the final solution are needed to achieve freedom from systematic effects due to variation in matrix. Ranges of 0% to more than 100% matrix variation for alumina, silica, and calcium were tested. When lanthanum was absent, lithium, sodium, potassium, and cesium each was incapable of totally eliminating the effects of aluminum on emission. Silica addition to the fusion helps achieve proper flux viscosity to aid removal of the fused bead from graphite crucibles.

A dual-tube sample-introduction system involving a peristaltic pump permits flexible addition of spectrochemical buffer or releasing agent, and substantial time saving. Matrix effects and the applicability of buffers or mixed-solution releasing agents can be conveniently studied, even if the buffers would be unstable in mixed solutions.

Table 5. MAFLS (Mississippi-Alabama-Florida Shelf) samples.

Station No.	Description
2207	Fine-grained material (carbonate sand?) containing 33% shell fragments, small whole shells, and dark gray-black inclusions (specks).
2208	Mixture of shells, coral, and pieces of crab or worm burrows graded from 1-cm-long fragments to very fine particles.
2209	Very fine light-gray material (carbonate sand?) containing a few small shell fragments.
2317	Mixture of medium to coarse shell fragments containing 10% dark-gray-black inclusions.
2427	Fairly homogeneous, light-grayish-brown medium to fine material.
2531	Mixture of coarse to fine shell and coral or worm-burrow fragments.
2638	Dark-grayish-brown medium to fine material containing a few white shell fragments.
2639	Dark-grayish-brown medium to fine material containing 10% shell fragments.
2957	Fine, light-brown fairly homogeneous material containing some medium-size shell and coral fragments.
2960	Medium to fine black and white material (ground pepper).

Table 6. Ba content determined by two runs of duplicate aliquots of marine sediment samples.

Sample set/no.	Mean Ba content (μg/gm)	Standard deviation
CSA 128 A-1	33	1.5
CSA 129 A-2	29	1.2
CSA 130 B-3	64	2.6
CSA 131 B-4	24	2.4
CSA 132 C-5	17	2.1
CSA 133 C-6	15	1.0
CSA 134 D-7	11	1.0
CSA 135 D-8	37	2.8
MAFLA 2207	54	4.5
MAFLA 2208	14	1.2
MAFLA 2209	30	1.1
MAFLA 2317	19	2.0
MAFLA 2427	49	2.2
MAFLA 2531	16	1.8
MAFLA 2638	305	8.1
MAFLA 2639	90	7.0
MAFLA 2957	18	1.6
MAFLA 2960	13	1.0

The effect of refractory-substance formers such as aluminum with calcium can be reduced or removed by selection of high-temperature parts of the arc, but we chose not to pursue this alternative because of significant loss in analytical sensitivity and the need for greater precision in optical adjustment.

The analysis of standard rock samples -- andesite, basalt, marine mud, and shale of the Green River Formation -- by the method described in this paper showed generally very satisfactory agreement with precision methods of analysis, such as isotope dilution and X-ray fluorescence.

Analysis of a series of carbonate-rich sedimentary samples sent to us by CSA and BLM showed generally very low Ba values in the range 11-60 ppm, though one sample contained 330 ppm Ba. The low Ba content suggests that these samples are of carbonate-ooid-reefal sediments. Although the MAFLA samples were coarse and inhomogeneous, Ba contents of splits did not show significant disagreement. Ba concentration coherence was much closer for splits of the apparently inhomogeneous samples than for separate samples from specific sites.

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