

THE DETERMINATION OF ARSENIC, ANTIMONY,  
SELENIUM AND TELLURIUM IN ENVIRONMENTAL WATER  
SAMPLES BY FLAMELESS ATOMIC ABSORPTION

By

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### BRIEF

Total arsenic, antimony, selenium and tellurium have been determined in environmental samples without the need for prior digestion. The method of standard additions was required in order to correct analytical results for observed interferences. Recoveries ranged from 90% to 110% at a concentration of 10 $\mu$ g/l for individual metals.

## ABSTRACT

A method has been developed for the direct determination of arsenic, antimony, selenium, and tellurium in surface waters and industrial effluents using the graphite furnace. Optimization of instrumental variables is discussed. Representative inorganic acids enhanced the analytical signal of arsenic, antimony, and tellurium, and suppressed the response of selenium. The effect of alkali and alkaline earth elements, commonly present in environmental samples, on the determinations have been studied and their interferences documented. These investigations showed that for valid analytical results experimental variables must be closely controlled, and the method of standard additions is required. The results of the developed procedure were compared to the hydried generation technique for arsenic and selenium on real samples. Recoveries ranged from 90% to 110% at a concentration of 10 $\mu$ g/l for individual metals.

## INTRODUCTION

Currently, flame atomic absorption spectrophotometry is usually the method of choice in characterizing environmental samples for trace metals. The proposed interim drinking water standards (1) set maximum permissible concentrations of 50 $\mu$ g/l and 10 $\mu$ g/l for arsenic and selenium, respectively, and the United States Public Health Service (2) recommends an acceptable arsenic level of 10 $\mu$ g/l. The United States Environmental Protection Agency (U.S.EPA) approved procedure for total metals (3) requires acid digestion of samples prior to the analytical measurements. Since direct flame atomic absorption procedures fall short of the required sensitivities for the above metals, the U.S. EPA is promulgating the hydride generation - atomic absorption method. However, this technique also requires wet oxidation of samples prior to analytical measurements and can thus be slow and subject to volatilization losses of the elements of interest.

Flameless atomic absorption spectrophotometry has the capability to determine total metals without chemical pretreatment, provided the aqueous phase can be sampled in a reproducible manner. Electrically heated furnace units, commercially available from several manufacturers, are finding wider acceptance in the characterization of environmental samples for trace elements (4-9). Their application to filtered (5) and relatively clean (4, 7, 8) waters have been reported.

This study was undertaken to demonstrate the applicability of flameless atomization methods to the determination of total arsenic, antimony, selenium, and tellurium in surface waters and industrial effluents without prior digestion.

Well mixed samples are injected directly into the furnace. Although interferences, i.e., suppression or enhancement of a spike signal by a matrix compared to the corresponding response in a matrix-free standard, are observed, the application of the standard additions method provides valid analytical data for all metals investigated.

## EXPERIMENTAL

Apparatus. A Perkin-Elmer Model 503 atomic absorption spectrophotometer equipped with a deuterium background corrector, an HGA-2100 or HGA-2000 heated graphite atomizer, electrodeless discharge lamps (EDLs), and a strip chart recorder was used for all analytical measurements. Table I lists the instrumental settings. The auto-interrupt gas flow mode was applied for all determinations.

Eppendorf pipets were used for all volume measurements and furnace sample injections. Polystyrene cups were procured commercially (Instrumentation Laboratory, Inc.).

Reagents. Arsenic, antimony, selenium and tellurium certified atomic absorption standards (1000  $\mu\text{g/ml}$ ) were obtained commercially (Fisher Scientific Co. and Varian Instrument Div.). Working standards were prepared by serial dilutions of the concentrates using distilled, deionized water and reagent grade acids. Prepurified grade argon was used as the purge gas during sample analysis.

Procedure. All reported data were obtained by the method of standard additions. In general, equal volumes of a well mixed sample and a working standard or blank were prepared in 1 ounce polystyrene cups. A 100  $\mu\text{l}$ -aliquot of each of the series of solutions was injected into the furnace to generate a linear working curve. Metal concentrations were derived from either graphical extrapolations or linear regression calculation routines. The standards employed ranged in concentration from 0 to 10  $\mu\text{g/l}$ .

The hydride generation results were obtained by standard U.S. EPA approved procedures (3).

## Results and Discussion

Furnace Optimization. Preliminary HGA furnace operating parameters provided by Perkin-Elmer Corp. (10) appeared to be less than optimum according to our observations and those of others (5,6). As a consequence, experiments were performed to generate charring temperature - absorbance relationships for the elements under study. These results are presented for inorganic standards in Figure 1. The data show that in a 1% nitric acid medium ashing temperatures of 700°C for tellurium and 1000°C for arsenic, antimony and selenium can be used without a significant loss of signal. The use of maximum permissible charring temperatures is of advantage in flameless atomization techniques for minimizing non-specific absorption interferences due to incomplete volatilization of organic components. Figure 2 presents ashing temperature - absorbance profiles for three organoarsenic compounds. No losses were observed up to 1400°C.

Sensitivities were found to be independent of atomization temperature for the above metals. Therefore, all elements but antimony were analyzed at the maximum furnace temperature of 2700°C in order to insure the removal of less volatile components that may show a cumulative interference during sample analyses. An atomization temperature of 2200°C was chosen for antimony, since at higher settings non-specific furnace peaks were observed.

Interferences. Figures 3, 4 and 5 show absorbances of 10 µg/l standards as a function of acidity for hydrochloric, nitric, and sulfuric acids, respectively. All acids exert a positive and concentration dependent

interference for arsenic, antimony, and tellurium, while a suppression effect is observed for selenium. Selenium could in fact not be successfully recovered from any of the sulfuric acid standards due to severe background absorptions that exceeded the background correction capabilities of the instrument. While the theoretical aspects of this behavior are as yet unknown, the results indicate that for valid and reproducible data close control over acidities must be exercised. As a consequence, the proposed analytical procedure incorporates mixing of samples and standards prior to furnace injection.

Matrix interferences due to cations at concentrations normally found in surface waters and industrial effluents were also studied. Table II summarizes the data for the alkali and the alkaline earth metals. Selenium was not investigated in detail, since our experience coincides with matrix effects reported in the literature (6) for this element. These results show that suppression and enhancement effects are observed, which are in general a function of interferant concentration and element determined. No interferences were observed for cobalt, copper, lead and manganese up to 1 mg/l and iron up to 10 mg/l. Several investigators have used matrix separation by either ion exchange (6) or liquid-liquid extraction (9) prior to analysis. These procedures are lengthy and are subject to incomplete recoveries, considerations that are of importance to high-volume environmental laboratories.

Comparability and Recovery Studies. Table III lists comparative data for arsenic and selenium on representative water samples by the graphite furnace and the hydride generation methods. The results show a satisfactory



agreement and indicate the applicability of the furnace technique for total metal determinations without prior digestion in most cases. However, some samples may contain a matrix that would significantly suppress the analytical signal of the metal at the concentration of interest. As a general rule, if this suppression exceeds approximately 75% of the original spike standard, a wet oxidation step prior to analysis becomes mandatory for valid results. Table IV assesses the precision of the method at two concentration levels. This data was obtained by repetitive injections of unspiked and spiked samples, and reflects the reproducibility that can be expected on actual samples. Results on recoveries are summarized in Table V. Standard addition procedures were used throughout, and the data are representative of results routinely obtained on surface waters and industrial effluents. Low level determinations of the metals under study were of primary interest; higher concentrations can be readily determined by appropriate adjustments of instrumental variables, i.e. wavelength, gas flow mode, or sample dilutions.

# ACKNOWLEDGMENT

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The use of trade names or commercial products does not constitute endorsement nor recommendation by the United State Environmental Protection Agency.

TABLE I

INSTRUMENTAL SETTINGS FOR THE DETERMINATION OF  
ARSENIC, ANTIMONY, SELENIUM AND TELLURIUM

	As	Sb	Se	Te
Wavelength, nm	193.7	217.6	196.0	214.3
Bandpath, nm	0.7	0.2	0.7	0.7
√EDL Power, W	8	8	6	9
Drying Temp., °C(Time,sec)	125(60)	125(60)	125(60)	125(60)
Charring Temp., °C (Time,sec)	1000(40)	1000(40)	1000(40)	700(40)
Atomize Temp., °C(Time,sec)	2700 (5)	2200 (5)	2700 (3)	2700 (5)
Argon Gas Flow, ml/min	50	50	50	50

TABLE II

Effect of the Alkali and the Alkaline  
Earth Metals On 10  $\mu$ g/l of As, Sb, and Te

% enhancement (+) or suppression (-) on the  
absorbance of a 10 $\mu$ g/l solution containing As, Sb &

Element	Conc. of interfering metal, mg/l	Ca	K	Mg	Na
As	50	0	-5	+23	-6
Sb		+9	-10	+5	+7
Te		-19	+5	-7	0
As	100	-5	-10	+21	0
Sb		+4	-3	+3	-7
Te		-13	+15	-23	+10
As	250	+5	-11	+17	+8
Sb		+5	-6	+2	+2
Te		-22	+3	-26	0
As	500	+6	-10	+20	+7
Sb		-3	+8	+11	+2
Te		-18	0	-26	-12
As	750	+7	-11	+15	+13
Sb		+2	+4	0	0
Te		-14	-20	-33	-14
As	1000	+9	-15	+22	+4
Sb		-2	+5	+4	0
Te		-17	-30	-35	-17

TABLE III

Comparison of the Furnace and the Hydride Generation Methods  
In the Analysis of Environmental Samples for Arsenic and Selenium

Type of Sample	As, $\mu\text{g/l}$		Se, $\mu\text{g/l}$	
	Furnace	Hydride	Furnace	Hydride
Metals Industry	16	14	13	14
	12	12	14	14
	24	28	13	16
	16	13	14	14
	13	12	13	12
	20	20	13	11
Power Plant	14	10	12	11
	14	12	11	12
	14	12	12	13
	14	12	15	13
Sewage Treatment Plant	10	12	13	13
	10	14	15	12
	11	12	10	13
	11	10	11	12
	10	12	12	13
	10	12	11	13
S. D. of Diff., $\mu\text{g/l}$ (11)	1.7		1.2	

TABLE IV

Precision of the Flameless Atomization Method  
As a Function of Concentration

Element	Concentration, $\mu\text{g/l}$	n	S.D., $\mu\text{g/l}$	Rel.S.D., %
As	2.5	12	0.2	8.0
	10.0	16	0.3	3.0
Sb	2.5	15	0.1	4.0
	10.0	15	0.3	3.0
Se	3.0	8	0.2	6.7
	10.0	13	0.5	5.0
Te	2.5	15	0.1	4.0
	10.0	15	0.4	4.0

TABLE V

Recovery of Arsenic, Antimony, Selenium  
And Tellurium from Environmental Samples

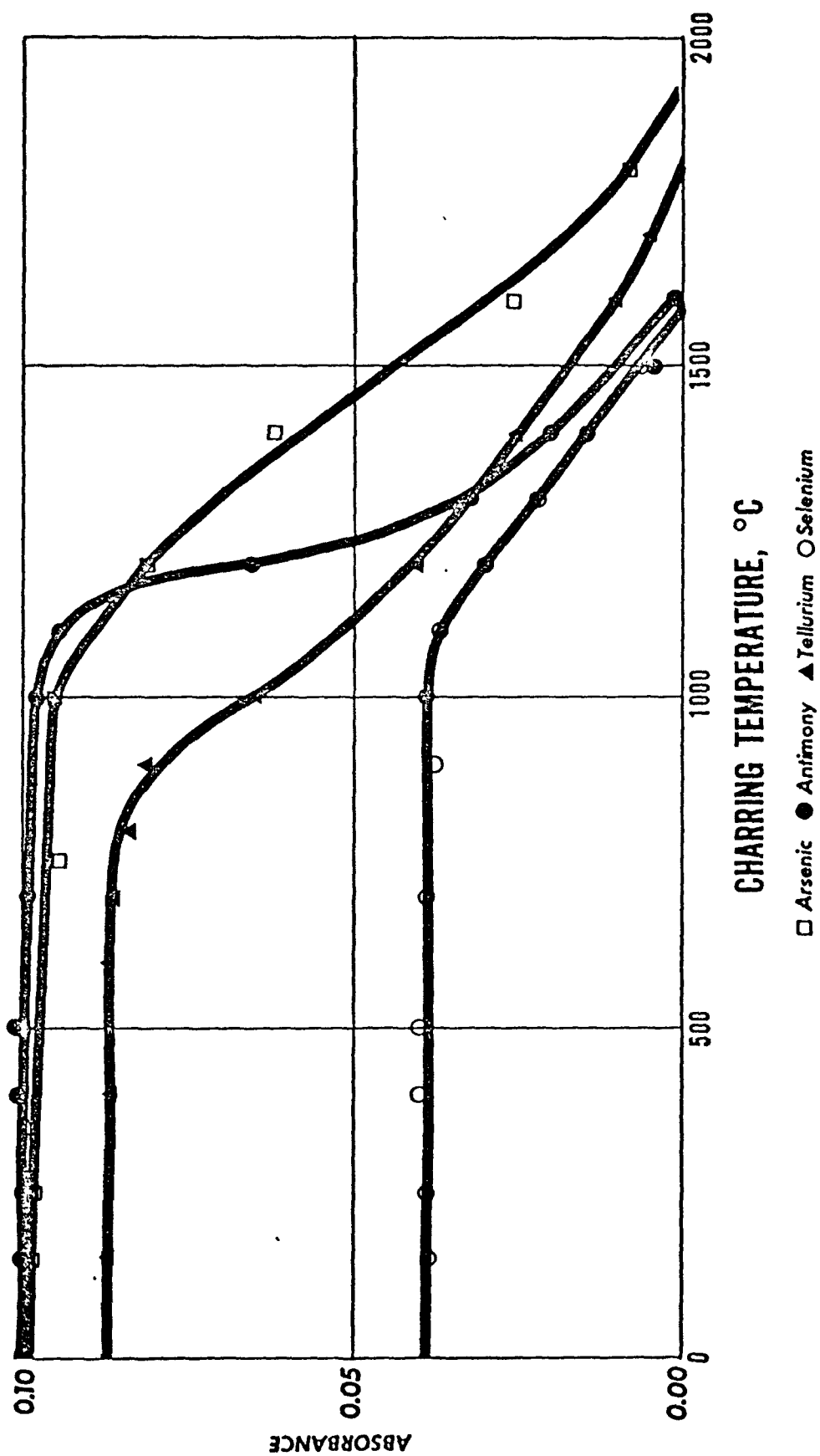
Type of Sample	Conc. of Metals Added, $\mu\text{g/l}$	As, $\mu\text{g/l}$			Sb, $\mu\text{g/l}$			Se, $\mu\text{g/l}$			Te, $\mu\text{g/l}$		
		Initial	Final	Rec., %	Initial	Final	Rec., %	Initial	Final	Rec., %	Initial	Final	Rec., %
Metals Industry	10.0	<1.0	10.5	105	<2.0	10.0	100	1.0	11.0	100	<1.0	10.0	100
	10.0	13.0	22.0	90	5.0	14.5	95	3.0	14.0	110	2.0	12.5	105
	10.0	3.0	12.0	90	<2.0	10.0	100	4.0	15.0	110	<1.0	9.5	95
	10.0	1.0	10.5	95	<2.0	9.5	95	<1.0	9.5	95	<1.0	9.0	90
	10.0	2.5	13.0	105	3.0	12.0	90	3.0	13.0	100	<1.0	10.0	100
Power Plant	10.0	1.0	11.0	100	<2.0	10.0	100	1.0	11.0	100	<1.0	10.5	105
	10.0	1.0	10.0	90	<2.0	10.0	100	1.0	11.0	100	<1.0	10.0	100
	10.0	1.5	10.5	90	<2.0	9.5	95	1.0	12.0	110	<1.0	10.5	105
	10.0	2.0	11.0	90	4.0	13.0	90	4.0	14.0	100	2.0	12.0	100
	10.0	2.0	12.0	100	3.0	12.5	95	<1.0	10.0	100	2.0	13.0	110
Sewage Treatment Plant	10.0	2.0	11.0	90	3.0	12.0	90	<1.0	10.0	100	<1.0	9.5	95
	10.0	2.0	12.0	100	3.0	13.5	105	6.0	15.5	95	2.0	11.5	95
	Sensitivity, g(absolute) D.L. <sup>a</sup> , $\mu\text{g/l}$ (relative)		$3.0 \times 10^{-11}$		$3.0 \times 10^{-11}$	$5.0 \times 10^{-11}$		$4.0 \times 10^{-11}$					
			0.5		2.0	2.0		1.0					

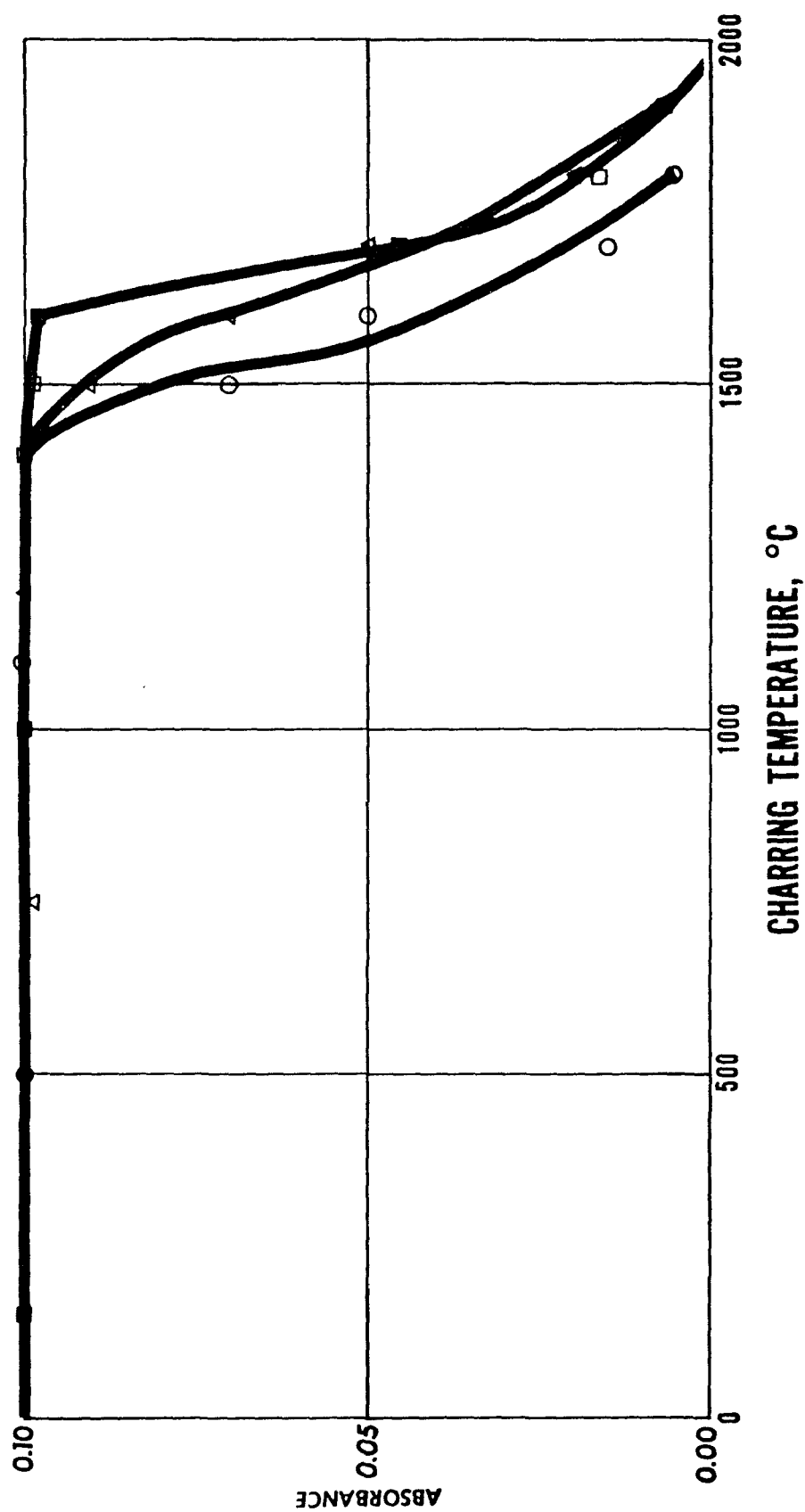
<sup>a</sup>D.L.: detection limit ; defined as signal:noise = 2



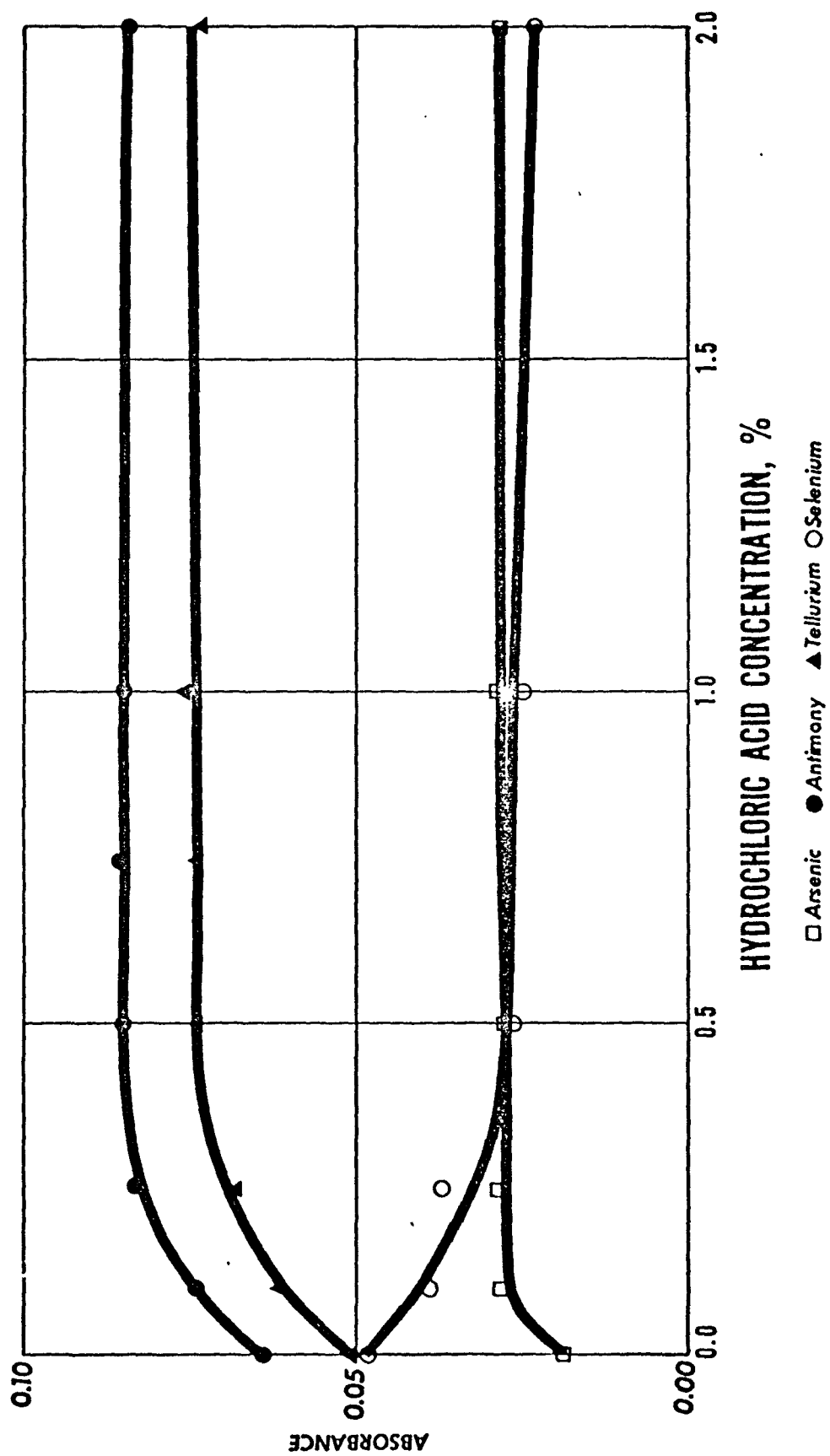
### FIGURE CAPTIONS

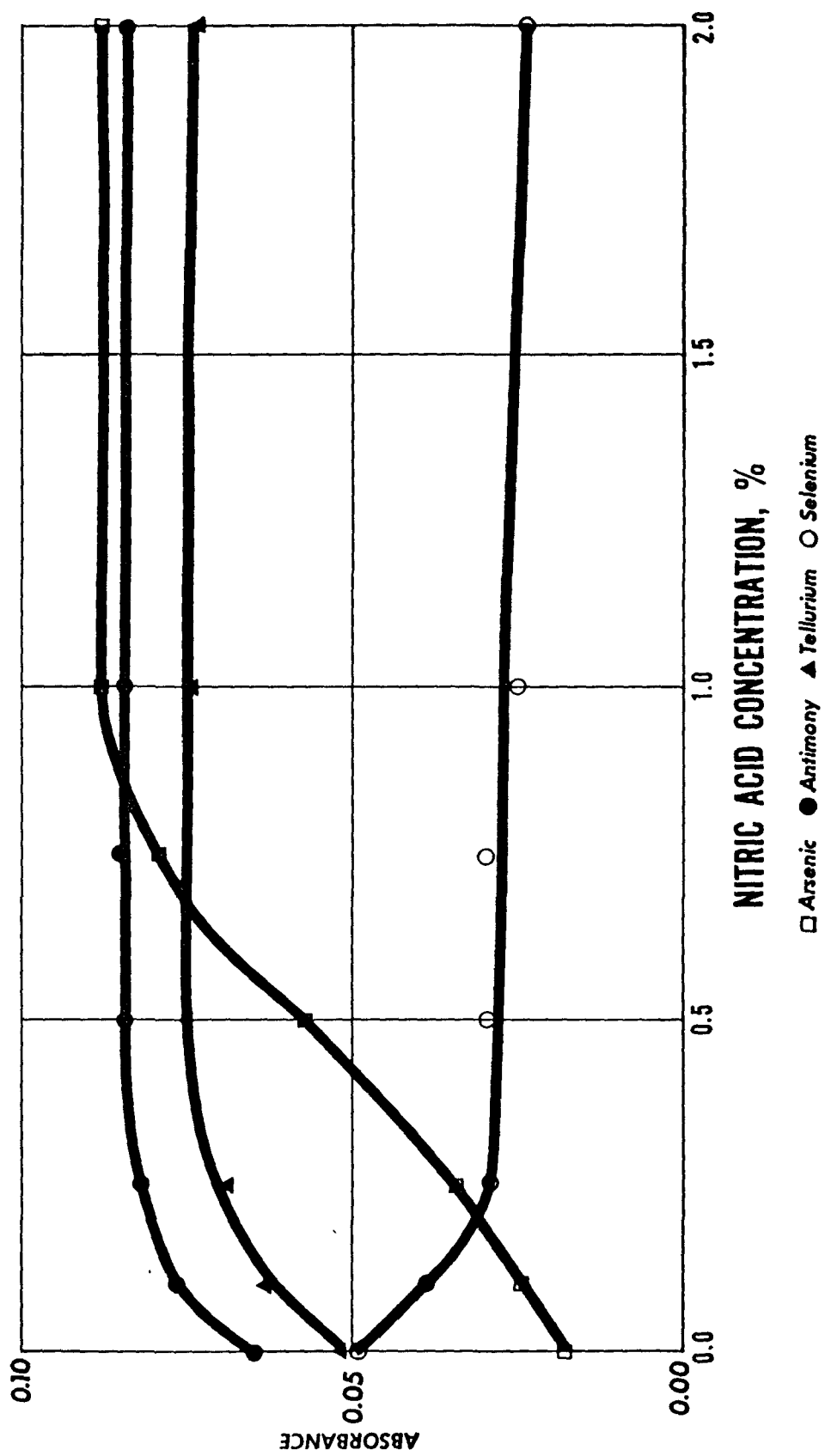
- Figure 1 - Absorbance as a function of charring temperature for inorganic compounds ( $10\mu\text{g/l}$ ). A temperature of  $1000^{\circ}\text{C}$  is optimum for arsenic, antimony, selenium and  $700^{\circ}\text{C}$  for tellurium.
- Figure 2 - Absorbance as a function of charring temperature for organoarsenic compounds ( $10\mu\text{g/l}$ ). A temperature up to  $1400^{\circ}\text{C}$  provides for quantitative recovery.
- Figure 3 - Absorbance as a function of hydrochloric acid concentration. Arsenic, antimony and tellurium are enhanced, selenium is suppressed.
- Figure 4 - Absorbance as a function of nitric acid concentration. Arsenic, antimony and tellurium are enhanced, selenium is suppressed.
- Figure 5 - Absorbance as a function of sulfuric acid concentration. Arsenic, antimony and tellurium are enhanced, selenium is totally suppressed.





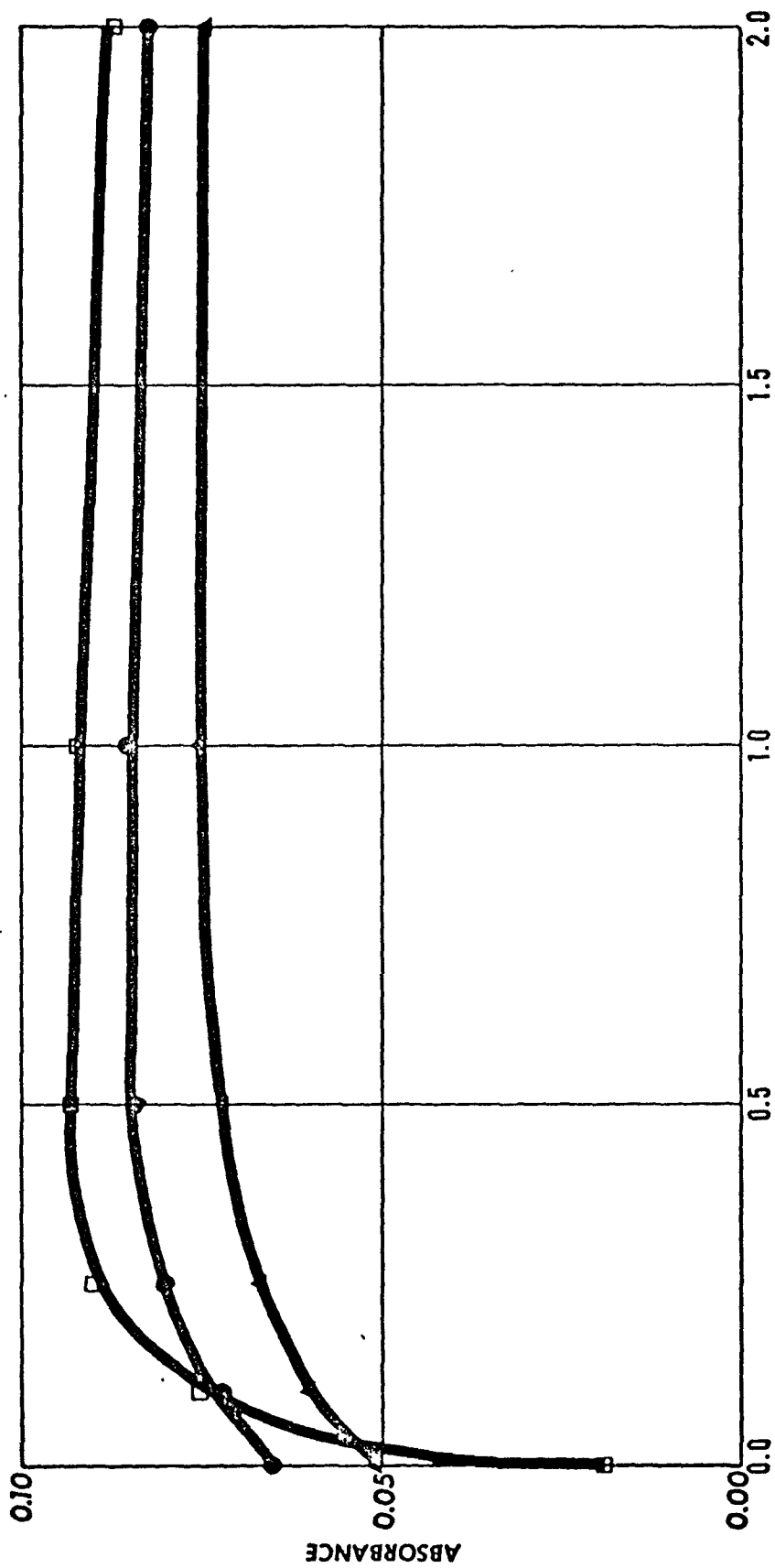
□ p-Arsanilic Acid ○ Triphenylarsine △ Ethylenebis - (diphenylarsine)





One

Letter to the Editor  
1977  
2000  
2000



□ Arsenic   ● Antimony   ▲ Tellurium   Selenium was not recovered

