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The atomic absorption determination of ultra-trace tellurium in rocks utilizing high sensitivity sampling systems

Richard D. Beaty

Department: Chemistry

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THE ATOMIC ABSORPTION DETERMINATION OF ULTRA-TRACE TELLURIUM IN ROCKS UTILIZING HIGH SENSITIVITY SAMPLING SYSTEMS

by

RICHARD DUANE BEATY, 1945-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

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O K Manuel
Advisor

Wm. H. Webb

D W Beistel

Wm R Carroll

Charles A Sorrell

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To My Wife

ABSTRACT

The sampling boat and the graphite furnace have been shown to possess the required sensitivity to detect tellurium at ultra-trace levels, in a variety of sample types, by atomic absorption. In the sampling boat approach, tellurium in sample solutions is chemically separated and concentrated by extraction into methyl isobutyl ketone before measurement. For samples exhibiting extraction interferences or excessively high background absorption, a preliminary separation of tellurium by coprecipitation with selenium is described. Using this technique, tellurium can be quantitatively detected down to 5 nanograms and linear response is observed to 100 nanograms. Relative standard deviations of better than 7% are achieved for 50 nanograms of tellurium. For samples which have a tellurium content below the detection limits of the sampling boat, the graphite furnace is used for atomization. By this method, as little as 0.07 nanograms of tellurium can be detected, and a precision of 1% relative standard deviation is achievable at the 5 nanogram level. A routinely applicable procedure was developed for determining tellurium in rocks, using the graphite furnace, after a hydrofluoric acid decomposition of the sample. Using this procedure, tellurium data were obtained on 20 different rocks, and the significance of this new information is discussed.

ACKNOWLEDGMENTS

The author gratefully acknowledges his indebtedness to his advisor, Dr. Oliver K. Manuel, whose capable guidance and constant encouragement brought this work to this final stage. I must also express special appreciation to Dr. W. H. Webb, Dr. W. R. Carroll, and Dr. G. L. Bertrand, whose helpful advice and direction influenced the course of my life long before this work ever commenced.

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My appreciation and love go to my wife for enduring the trials and tribulations involved in raising a family under less than ideal circumstances during the course of my education. An equally sincere gratitude goes to my parents, without whose support and encouragement throughout my life, this dissertation would never have been a reality.

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I. INTRODUCTION

Until recently, tellurium has occupied a rather obscure position on the periodic table of the elements. As a metal, tellurium has spawned no economic interest, due to its lack of strength and hardness. The "useless metal" was investigated as a gasoline additive for its anti-knock properties, but it was soon realized that such a use, even at low concentration, would rapidly exhaust known supplies of the element. Tellurium has found some use as a coloring agent for glass, giving a blue to brown color, and more recently, its electrical properties are being utilized by the semi-conductor industry. The most famous property attributed to element number 52, however, has been the phenomenon of "tellurium breath", which many of the early workers acquired as their reward for scientific curiosity.

In spite of the rather indifferent attitude toward tellurium in the past, interest in this element is now developing in several fields. Tellurium is known to be toxic, but the extent of its toxicity is largely speculative. More serious efforts are now being undertaken by several institutions to more accurately classify the effect of tellurium on living organisms. It has recently, for instance, been suspected as a possible carcinogen, and studies on this property of tellurium are now in progress[1].

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[1] H. Issaq, Litton Bionetics, personal communication (1973).

Several potential biological and biochemical problems concerning tellurium suggest themselves from information obtained on a somewhat more thoroughly studied sister element, selenium. Selenium has been found to be present to a surprising extent in plants, and it appears to play a definite nutritional role in plant growth[2]. Some plants concentrate selenium to a level which is dangerous to livestock feeding on them. The chemical similarities of selenium and tellurium prompt speculation that the latter may also be playing a role in this area, but the increased scarcity of tellurium has put a strain on analytical techniques to detect trace, but possibly significant, variations of the element.

The United States Department of Agriculture is now undertaking an extensive investigation of analytical techniques for determining selenium in food products, which may originate naturally or from additives in fertilizer and feeds[3]. A similar effort might be anticipated for tellurium as a natural extension of the work already in progress.

A yet unmentioned field of interest in tellurium is geochemistry. Tellurium has been studied in mineral deposits, where the tellurium content is high[4], but general distribution data on tellurium in the earth's crust is conspicuously absent. This lack of data is due to the

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[2] I. Rosenfeld and O. A. Beath, "Selenium Geobotany, Biochemistry, Toxicity, and Nutrition", Academic Press, Inc., New York (1964).

[3] F. Dalton, USDA, personal communication (1973).

[4] F. D. Everett, U.S. Bureau of Mines Report No. 6350 (1964).

extreme scarcity of tellurium and the lack of an analytical method possessing the sensitivity required to detect the trace amounts present. The association of tellurium with gold is well known. A fast and reliable method for determining trace tellurium in geological materials would facilitate the use of tellurium as a "path-finder" element for gold in geochemical exploration.

In addition to the economic potentials for exploiting tellurium analyses, a ripening environmental concern exhibits a need for monitoring the presence of this toxic element. While the overall tellurium abundance is low, local concentrations in ores of economic importance may be redistributed through the air and water by mining operations, posing an unknown threat to public health in those areas. A more widespread potential hazard exists from the possible introduction of tellurium into the air from the burning of tellurium-containing coals.

Before any judgments could be made on how man has altered the natural distribution of tellurium, it would be necessary to ascertain its natural distribution. The purpose of this study was to develop an analytical method for the determination of ultra-trace quantities of tellurium in geological materials and to show that the method would be applicable to determining an environmental baseline for tellurium. Of the possible approaches, atomic absorption was selected because of its speed and specificity. Relatively new high sensitivity sampling devices gave atomic absorption the potential for detecting the required ultra-trace levels. The manuscript presented in Section II of this dissertation entitled "Atomic Absorption Determination of Nanogram Quantities of Tellurium Using the Sampling Boat Technique", was published in Analytical Chemistry. In this section, the sampling boat technique is explored for its application to tellurium analysis, and a useful method for determining nanogram amounts of tellurium in a wide variety of sample types is given. This technique, however, fell short of the requirements necessary to accomplish the above objective. Further studies on other trace sampling techniques resulted in the manuscript "Atomic Absorption Determination of Sub-Nanogram Quantities of Tellurium Using the Heated Graphite Atomizer", which is presented in Section III. This paper has been submitted to Analytical Chemistry as a sequel to the sampling boat work. It describes the use of a flameless sampling device, which exhibits the ability to successfully detect tellurium at the parts per billion level in rocks. The final section of this dissertation, "Tellurium in Rocks", has been submitted to Chemical Geology for publication. This manuscript presents tellurium data gathered on some representative rock types using the methodology developed and described in Section IV. The geological significance and correlation of this data with earlier estimated tellurium values are discussed.

II. ATOMIC ABSORPTION DETERMINATION OF NANOGRAM QUANTITIES OF TELLURIUM USING THE SAMPLING BOAT TECHNIQUE

by

Richard D. Beaty

Manuscript as published in Analtyical Chemistry, **45**, 234 (1973).

BRIEF

Two chemical procedures are given for determining as little as 5-10 nanograms of tellurium with relative standard deviations of 5.0% and 6.6%. Interferences and ways of eliminating them are discussed.

ABSTRACT

A method for the determination of ultra-trace quantities of tellurium has been developed, utilizing the sampling boat technique of atomic absorption. Two procedures were developed for the chemical separation of tellurium. In some types of samples the tellurium can be directly extracted from 4 M HCl solution into methyl isobutyl ketone. The relative standard deviation obtained for a typical sample treated in this manner and analyzed by atomic absorption was 5.0%. In samples where other constituents cause chemical interference with the extraction, a preliminary separation of tellurium by coprecipitation with selenium was employed. The relative standard deviation using this procedure increases to 6.6%, but few interferences are observed. Linear response occurs for a range of 5-100 ng tellurium.

The ability to accurately analyze very small amounts of tellurium has become important with the arrival of an increasing awareness of trace constituents in the environment. While tellurium is regarded as toxic, the toxicological properties of trace quantities of this element are generally unknown. A sister element, selenium, has been found to have a wide distribution in plants (1), and this occurrence of selenium is attributed with having caused many livestock poisonings in western United States. While a similar study of tellurium has never been undertaken, it is logical to assume that this element could, at least, be a cocontributor in such incidents. Selenium has, also, been shown to exhibit interesting effects as an antidote for mercury poisoning (2), which prompts more interest in the unexplored toxic and nutritional role of trace amounts of tellurium.

Another area in which reliable trace tellurium analyses would be of value is in the field of geochemistry. Data on the distribution of tellurium in the earth's crust is virtually nonexistent, except in areas of tellurium mineral deposits. More information on tellurium distribution would permit a better understanding of the geochemistry of this element.

Existing methods for low-level tellurium determinations leave room for improvement. An analytical method for determining the general distribution of this relatively rare element in the environment would require the utmost sensitivity in the lower parts per billion range. The difficulty in sample decomposition of geological materials would limit the sample size to no more than one gram, and thus, the method would have to be sensitive to a few nanograms of tellurium. Photometric methods are generally not sensitive enough and are subject to too many interferences to be seriously considered. Fluorescence has been used for tellurium at the nanogram level (3, 4), but with the inconvenience of working at liquid nitrogen temperatures. Tiptsova-Yakovleva et al. (5) report using A. C. polarography to achieve a tellurium sensitivity of about 50 ng/ml in the determination of cadmium and zinc tellurides, but electrolyte conditions are critical and would present a formidable separation problem in geological samples. Several papers have dealt with neutron activation determinations of nanogram quantities of tellurium (6, 7, 8, 9), but as reactors are not readily available to all analytical laboratories, a more widely employable method was sought.

Atomic absorption has been utilized for tellurium analysis (10, 11, 12), with the main problem being the quality of the hollow cathode lamps. The high noise level of the tellurium lamp has necessitated using a low scale expansion and has, thus, limited the sensitivity. However, Kahn et al. (13), in a report on the sampling boat technique, state that tellurium should be detectible down to 10 ng with the sampling boat accessory. Since interferences in atomic absorption are generally few, this method was selected for further investigation. Thorough discussions of the sampling boat technique appear in Kahn (13) and Luecke and Emmermann (14).

EXPERIMENTAL

Apparatus. Absorption measurements were made with a Perkin-Elmer Model 305A atomic abosrption spectrophotometer, equipped with the deuterium arc background corrector, the sampling boat accessory, and a Perkin-Elmer Model 56 recorder. A Perkin-Elmer tellurium hollow cathode lamp was used.

Tellurium absorption was measured at 214. 3 nm on a recorder range of 10 mv, with slit and damp settings of 3 and 1, respectively. The instrument expansion was adjusted for optimum signal to noise ratio.

Reagents. A standard 100 μg/ml tellurium solution was prepared by dissolving 100 mg pure tellurium metal in a minimum volume of HNO_3 plus about 2 ml HCl and diluting to one liter. More dilute standards were prepared by volumetric dilution of this solution.

A selenium solution for coprecipitation of tellurium was prepared and purified of tellurium by dissolving 600 mg selenium metal in a minimum volume of HNO_3 and taking to dryness. The residue was dissolved in 20 ml concentrated HCl, diluted to 60 ml with distilled water, and extracted with six 15 ml portions of methyl isobutyl ketone to remove tellurium contamination. The aqueous phase was then diluted to approximately 400 ml with distilled water, 5 grams hydroxylamine hydrochloride was added, and the solution was heated to boiling. After boiling for 2-3 hours, the selenium metal, which collected in the bottom of the beaker as one or two large pellets, was removed, washed with ethanol and water, dissolved in concentrated HCl plus a few drops of concentrated HNO_3, and diluted to 500 ml with distilled water. The final solution was approximately one mg/ml selenium.

Procedure. Two basic chemical procedures and either standard additions or a standard curve were used for sample analyses, depending on the nature of the sample and the expected tellurium content. When sample decomposition presented no problem and chemical interferences were not likely, the tellurium was extracted directly into methyl isobutyl ketone (MIBK) and an aliquot taken for analyses. Procedures for two samples of this type follow:

To determine tellurium in SeO_2, a one gram sample of SeO_2 was accurately weighed, dissolved in distilled water, and diluted to 100 ml. A 5 ml aliquot was pipeted into a 125 ml separatory funnel containing 45 ml of 4.5 m HCl, 10 ml MIBK was added and the tellurium was extracted by gentle shaking for 2 minutes. A 1 ml aliquot of the organic phase was introduced into the tantalum sampling boat, evaporated to dryness under a heat lamp, and inserted into the flame for the absorption measurement. The peak height produced by the recorder was compared to those of standards treated similarly to find the tellurium content of the sample.

When the sample contains large amounts of salt which might alter the extraction efficiency, the standard additions technique should be used. Such is the case in the following procedure for sulfuric acid.

Fifty ml of concentrated H_2SO_4 was pipeted into 100 ml of cold distilled water. The solution was kept cold in an ice bath while cold NH_4OH was slowly added to neutralize the acid to a methyl orange end point. Then, 170 ml concentrated HCl was added and the solution diluted to 500 ml, yielding a sample solution approximately 4 M in HCl. A 50 ml aliquot was transferred to each of five 125 ml separatory funnels, 0, 0.10, 0.20, 0.50, and 0.80 ml of 1 μg/ml tellurium solution were added, and the tellurium was extracted into 10 ml MIBK. A 1 ml aliquot of the extract was taken for the measurement. The peak heights were plotted against added tellurium and the line extrapolated to the concentration axis to find the tellurium content of the sample.

In samples where interferences were deemed likely and/or where the tellurium content of the sample was too low to allow the luxury of taking only a 1/10 aliquot of the extract, tellurium was preliminarily separated from the bulk of the sample by coprecipitation with selenium and subsequently extracted into only 1 ml MIBK. The analysis of tellurium in sphalerite is a typical example.

Sphalerite was selectively removed from a sample of sulfide ore and ground and sieved through an 80 mesh screen. Two 1 g samples of the -80 mesh fraction were weighed into 250 ml round bottom flasks, which were then joined to reflux condensers. Approximately 10 ml concentrated HNO_3 were added to each, and the mixtures were boiled under the reflux condensers for 10 minutes. To destroy the excess HNO_3, the heat was removed and formic acid added a few drops at a time until the reaction subsided. After the solutions had cooled, the condensers were rinsed into the flasks and removed, and the solutions were filtered through medium porosity paper into 250 ml beakers. Five ml of a 1 μg/ml selenium solution were pipeted into each and the samples were heated to boiling. Then, 5 ml 10% $SnCl_2$ in concentrated HCl (w/v) were added, and the solutions were boiled for 2 hours to digest the precipitate. After allowing to set overnight, the precipitates were centrifuged off in 50 ml centrifuge tubes and the supernatant solutions drawn off by suction through a finely drawn glass tube. The precipitates were washed once with distilled water, recentrifuged, and the liquid drawn off again. Two ml of concentrated HCl and one drop concentrated HNO_3 were added to each tube and heated in a hot water bath for the minimum time necessary for complete dissolution of the precipitate. The tubes were cooled, 3 ml of water and 1 ml MIBK were added, and the tellurium was extracted by vigorous swirling of the tube for 4 minutes. A 0.50 ml aliquot of the organic phase was taken for the absorption measurement. A reagent blank and standard curve were prepared by addin 0, 0.20, 0.40, 0.80 and 1.20 ml of a 0.100 μg/ml tellurium solution to 250 ml beakers and coprecipitating and extracting as above. The tellurium in the samples was determined by comparison to the standard curve.

RESULTS AND DISCUSSION

Extraction. An extraction procedure was desired in order to concentrate the tellurium from a dissolved sample and, thereby, maximize the sensitivity. Roth et al. (10) describe the extraction of microgram quantities of tellurium from 6 M HCl into MIBK. A preliminary investigation, in which aliquots of MIBK extract were analyzed by the sampling boat technique, showed that this extraction was quite successful for the extraction of down to 100 ng tellurium from 50 ml of HCl solution into 10 ml MIBK. A greater absorption was achieved, however, when extractions were from 4 M rather than 6 M HCl, so the lower acid concentration was adopted.

One ml of an aqueous solution containing 10 ng Te, the lower limit suggested by Kahn (13), gave a peak which was only slightly above background. However, the extraction increased the sensitivity by a factor of about five, and 5 ng became a realistic lower limit. Figure 1 shows the increased sensitivity achieved by the extraction. The reason for the sensitivity change is not entirely clear, since the solvent is evaporated before the measurement is made. It is assumed, however, that the extracted form of tellurium is more volatile than the aqueous species.

A heat lamp was used for evaporation of the solvent from the boat instead of the usual procedure of drying near the flame, as flammable MIBK will burn in the proximity of the flame. Burning the solvent led to low and erratic results, as would be expected.

Coprecipitation. For some samples, a direct extraction is not possible, due to chemical interferences in the extraction process. In these cases, a preliminary separation of tellurium from the bulk of the sample was accomplished by coprecipitation with selenium. The presence of selenium did not appear to affect the extraction of tellurium but did introduce a relatively high reagent blank due to tellurium contamination in the selenium, as shown in Figure 2. To minimize this effect, the smallest practical amount of selenium was used, and an effort was made to preliminarily remove the tellurium contamination. The most successful purification process proved to be the MIBK extraction described above. However, upon heating the aqueous phase to drive off suspended MIBK left after the extraction, there was a tendancy for the selenium to oxidize the finely dispersed organic material, resulting in an oily product which is not easily removed. This was minimized by adding a substantial amount of hydroxylamine hydrochloride to the solution after extraction and before heating to expel the organic suspension.

Various precipitating agents were tried in investigating the coprecipitation of tellurium with selenium. Stannous chloride gave the best results with respect to tellurium recovery. While recovery is not quantitative, it is proportional and complete enough to maintain a sensitivity of 10 ng. Figure 3 shows the effect of the coprecipitation on the method. The nonzero absorption of curve B for zero added tellurium is due to the reagent blank, which sets the lower limit of detection for the method. The decreased slope of curve B from curve A indicates tellurium recovery from the process is incomplete.

The amount of stannous chloride used for the precipitation is fairly critical. One gram resulted in a black sludge residue left in the sampling boat after evaporation of the solvent. The residue was presumed to be a reaction product of Sn(II) or Sn(IV) with MIBK. When only 100 mg was used, the precipitate was not readily separable from the solution, but 500 mg did give a manageable precipitate and minimized the sludge problem. The deuterium arc background corrector successfully compensated for the light scattering from small amounts of smoke due to the trace nonvolatile organic residue.

Interferences. A check for nitrate interference on the extraction was made to see if large amounts of this ion, which might be introduced during sample decomposition, would have a detrimental effect. Ten ml concentrated HNO_3 were neutralized with NH_4OH, added to 25 ml 8 M HCl, and diluted to 50 ml with distilled water. A 0.50 ml aliquot of a 1.00 μg/ml tellurium solution was added and the solution was shaken with 10 ml MIBK for 2 minutes. A 1 ml portion of the organic phase was taken for analysis and compared to a similar extraction without the nitrate. A nonvolatile yellow liquid residue remained in the bottom of the boat after evaporation of the solvent from the nitrate sample, and the peak height was greatly reduced. Also, large amounts of HNO_3 interferred with selenium precipitation when coprecipitation was tried. Therefore, when present, nitrate ion should be destroyed by formic acid reduction before proceeding with the coprecipitation or extraction.

In preparation for the analysis of tellurium in sphalerite and galena samples, direct extractions were tried in the presence of 100 mg quantities of zinc and lead. In both cases, tellurium recovery was greatly reduced, presumably through competition for the available chloride ion. The zinc case was particularly interesting in that a double peak occurred. The tellurium absorption at 214. 3 nm is dangerously close to the zinc absorption at 213. 9 nm. Therefore, it is likely that some energy absorption was occurring from extracted zinc, and the two peaks reflected the differences in volatilities of tellurium and zinc.

Surely many other metals would successfully compete with tellurium in the MIBK extraction, and it is advisable, therefore, to do the coprecipitation whenever metals are present. Both zinc and lead were found to exhibit no significant effects on the results when the coprecipitation procedure was used.

Arsenic and bismuth, two elements which might accompany tellurium through the coprecipitation process, were also checked for interference, and they introduced significant positive error into the coprecipitation procedure. However, when the As_2O_3 reagent which was used in the interference study was analyzed for tellurium by standard additions and direct extraction, the tellurium content indicated was equal to the positive error observed in the coprecipitation procedure. Also, the same amount of arsenic from a different bottle yielded a different value for tellurium when analyzed similarly. These two observations support the conclusion that the positive result obtained above for arsenic doped samples is attributable to tellurium contamination in the reagent, rather than an arsenic interference. A similar situation was assumed in the bismuth case.

The presence of arsenic did affect the extraction efficiency in a direct extraction, as evidenced by the decreased slope of the standard additions plot from the standard curve. The ability of standard additions and direct extraction to reproduce the value obtained by the coprecipitation procedure, however, illustrates that some interferences can be compensated for by standard additions without resorting to coprecipitation for actual elimination of the interfering species. When possible, this is a definite advantage, since the direct extraction can be performed in minutes, while the coprecipitation procedure requires 6-8 hours of working time with an overnight waiting period. The effects of the ions studied on the two procedures are shown in Table I.

Precision and Accuracy. The precision of both procedures was determined by measuring the peak heights obtained from 20 replicate determinations of 50 ng tellurium by direct extraction and by coprecipitation followed by extraction. The relative standard deviations of the 20 measurements were 5.0% and 6.6%, respectively.

The accuracy of the method was determined by analyzing a sample of known tellurium content. Since no samples were available with known parts per billion tellurium, a telluride with per cent level tellurium was dissolved in a mixture of HNO_3 and HCl (1:1) and diluted to appropriate tellurium levels. The telluride from Vatukoula, Fiji had been previously analyzed by conventional atomic absorption techniques by Srinivasan et al. (15), and a gravimetric determination of tellurium by stannous chloride reduction was performed for comparison. The results as determined by the various methods are shown in Table II. In addition to determining the tellurium content of the sample, portions of the sample solution were spiked with known amounts of tellurium, and the recovery from the coprecipitation process was determined by comparison to a standard curve. These results appear in Table III.

To establish the validity of the sulfide ore analyses, four 1 g samples of sphalerite were weighed into 250 ml round bottom flasks, spiked with 0, 0.2, 0.4, and 0.8 ml of 0.1 μg/ml tellurium standard, and treated as described in the procedure for sphalerite. The recovery of the tellurium spikes as determined by comparison to a standard curve is shown in Table III.

Other samples of low, unknown tellurium content were analyzed by the procedure outlined. The results of these determinations are summarized in Table IV.

Delves Cup Method. Since the development of the sampling boat technique, a modification of the same principle with even greater sensitivity has appeared. It was developed for the determination of lead in blood and consists of a small nickel cup, which is inserted into the flame under an open-ended ceramic tube, aligned so that the beam from the hollow cathode lamp passes through it. The volatilized material enters the tube through a hole above the cup and is momentarily retained, thereby increasing the sensitivity. The Delves cup method is described in detail by Fernandez and Kahn (16). The technique was tried for tellurium after MIBK extraction and showed an astounding sensitivity of 0.5 ng. Since the reagent blank encountered in the coprecipiprocedure, however, was an order of magnitude greater than this, the extra sensitivity was redundant, and the technique was not pursued further. When direct extraction is applicable, however, the Delves cup method would provide an ultra-sensitive tool for measurement.

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CREDIT

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Figure 1. Calibration curve for aqueous (A) and extracted (B) tellurium.

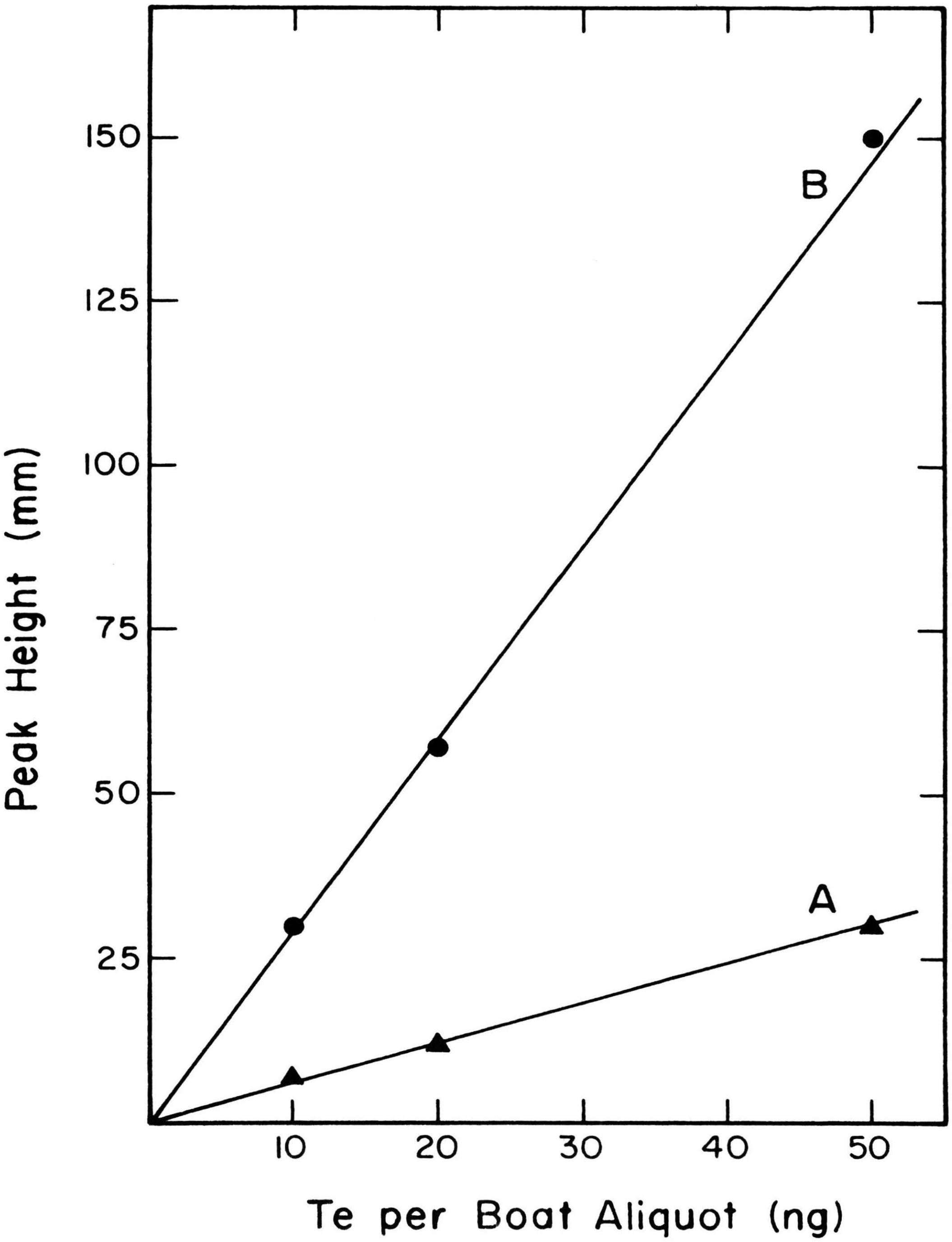
150
125
100
75
50
25
Peak Height (mm)
B
A
10
20
30
40
50
Te per Boat Aliquot (ng)

Figure 1

Figure 2. Effect of Se on extraction. Te standards with no Se (A) and with 5 mg Se (B) extracted into 1 ml MIBK. Intercept of line B extrapolation designates Te contamination in Se.

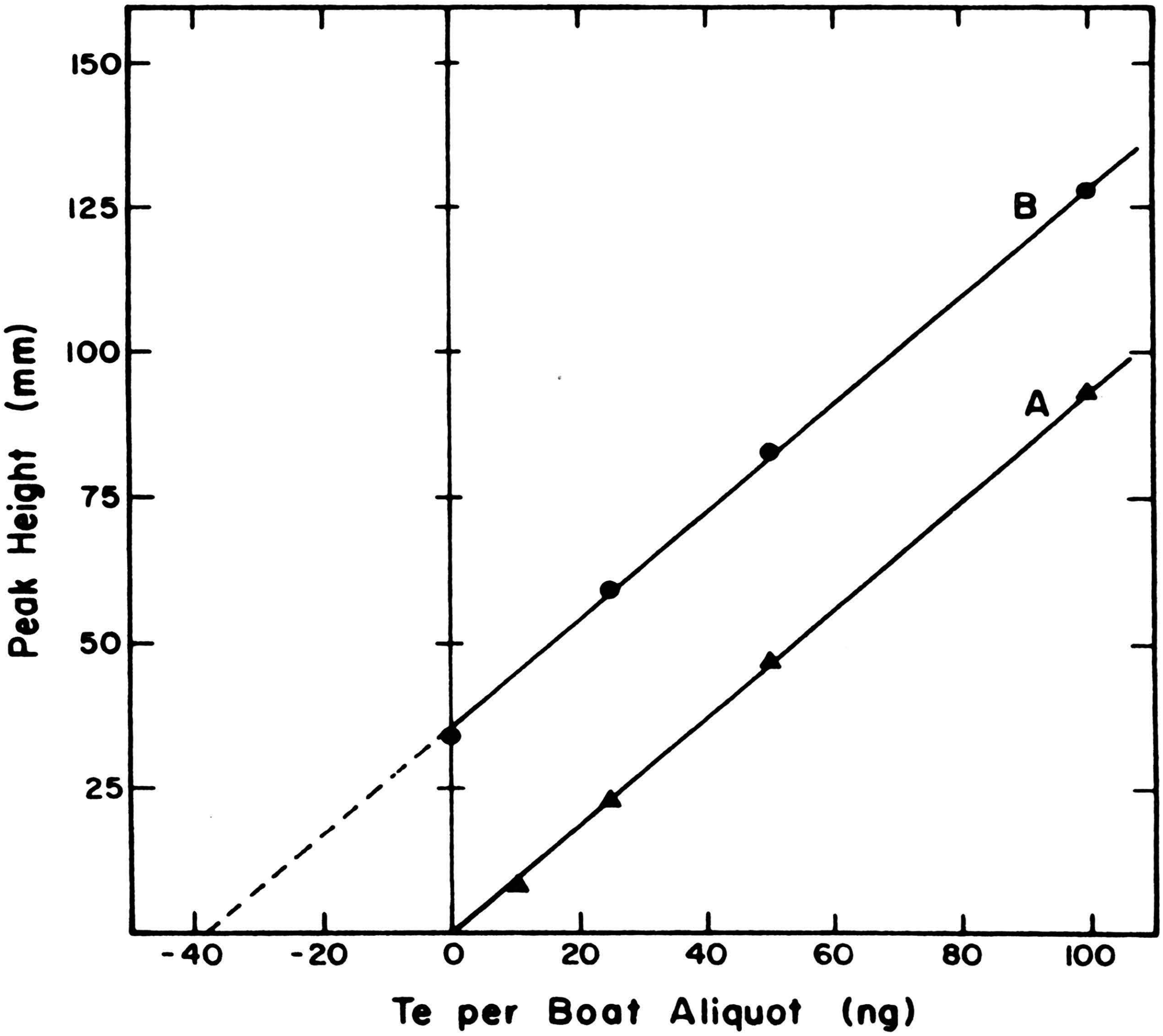
150
125
100
75
50
25
Peak Height (mm)
B
A
-40
-20
0
20
40
60
80
100
Te per Boat Aliquot (ng)

Figure 2

Figure 3. Effect of coprecipitation on Te recovery. Te standards directly extracted (A) and coprecipitated with 5 mg Se and then extracted (B).

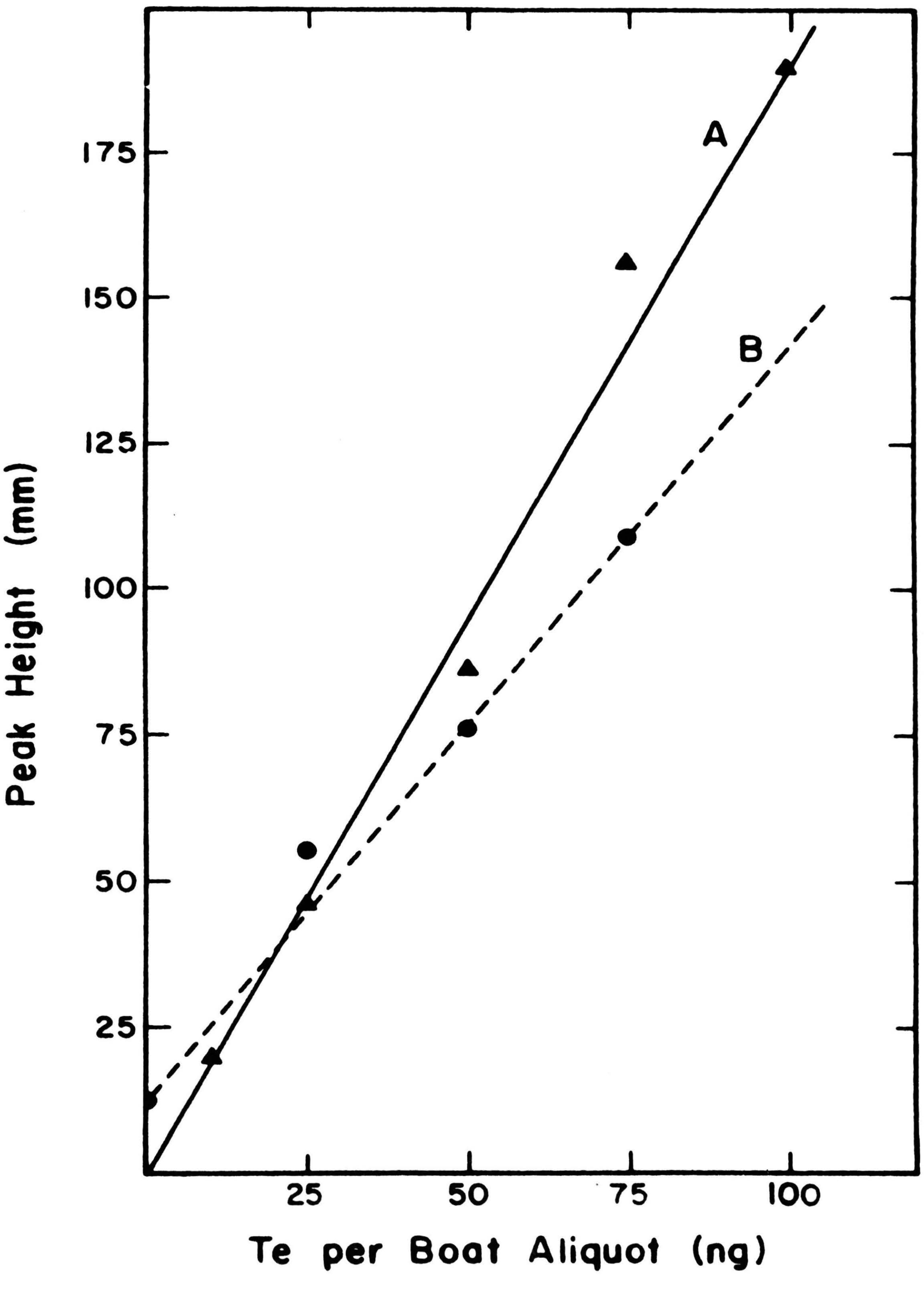
Peak Height (mm)
175
150
125
100
75
50
25
A
B
25
50
75
100
Te per Boat Aliquot (ng)

Figure 3

Table I. Diverse Ion Effects

Procedure	Ion	Amount	Te Added (ng)	Te Recov'd (ng)	Error (ng)	% Error
Direct Extraction	NO_3^-	3M	50	14	-36	-72
	Pb	100 mg	20	14	-6	-30
	Zn	100 mg	20	5	-15	-75
	As	100 mg	100	50*	-50	-50
Coprecipitation	Pb	100 mg	100	92	-8	-8
	Zn	100 mg	100	102	-2	+2
	As	100 mg	100	106*	-6	+6

*Corrected for Te contamination of reagent.

Table II. Analysis of Telluride from Vatukoula, Fiji

Method	% Te
Conventional Atomic Absorption*	33.7
Gravimetric Reduction	35.9
Direct Extraction, std. curve	33.5
Coprecipitation, std. curve	30.1
Coprecipitation, std. addns.	32.1

*Srinivasan, et al. (15)

Table III. Recovery of Te Spikes by Coprecipitation Procedure

Sample	ng Te Added	ng Te Found	Error (ng)	% Error
Telluride	200	190	-10	-5.0
	400	380	-20	-5.0
	800	760	-40	-5.0
Sphalerite	20	18	-2	-10.0
	40	45	+5	+12.5
	80	85	+5	+6.2

Table IV. Analysis of Samples

Sample	Procedure	Te Found
Se solution, 1 μg/ml (purified)	Direct Extraction, std. curve	1.7 ng/ml
Se metal	Direct Extraction, std. curve	4.3 p.p.m.
SeO_2	Direct Extraction, std. curve	2.9 p.p.m.
$SeOCl_2$	Direct Extraction, std. addns.	0.38 p.p.m.
H_2SO_4	Direct Extraction, std. addns.	57 p.p.b.
Sphalerite, A. L. Davis Mine (Ill.)	Coprecipitation, std. curve	130 p.p.b.
Galena, Blue Diggings Vein (Ill.)	Coprecipitation, std. curve	55 p.p.b.

III. ATOMIC ABSORPTION DETERMINATION OF SUB-NANOGRAM QUANTITIES OF TELLURIUM USING THE HEATED GRAPHITE ATOMIZER

by

Richard D. Beaty

Manuscript as submitted to *Analtyical Chemistry* (1973).

BRIEF

As little as 70 picograms of Te has been detected by flameless atomic absorption. A procedure is given for determining Te in rocks at the lower parts per billion level.

ABSTRACT

A flameless atomic absorption method for trace Te determinations has been developed. The temperature program and other parameters are given for measuring Te with the graphite furnace to a precision of better than 1% relative standard deviation at the 5 ng level. At the prescribed conditions, 30 pg of Te will give 1% absorption, and as little as 70 pg has been detected. A procedure is given for determining Te in rocks. After a hydrofluoric acid decomposition of the sample, standard additions are made to sample solution aliquots. The Te is extracted into methyl isobutyl ketone and injected into the graphite furnace, where it is dried, charred at 600°C and atomized at 2000°C.

INTRODUCTION

In order to undertake a project of determining the natural distribution of tellurium in the earth's crust, an analytical method was needed which was highly sensitive and sufficiently rapid and simple for routine application to a large number of samples. Several techniques based on neutron activation of tellurium appear in the literature (1-4), but because of interferences, most of these are not applicable to rock analysis. Those which are applicable require several weeks for completion and are somewhat lacking in sensitivity. Atomic absorption has been utilized to determine tellurium at the parts per billion level in sulfide ores using the sampling boat technique (5). However, the application of this method to general geochemical work is limited by the relatively high reagent blank, owing to a lengthy chemical separation, and by matrix problems which result from the decomposition of siliceous materials.

The extraordinary sensitivity of flameless sampling devices in atomic absorption have produced detection limits for metallic elements which rival and, in some cases, surpass those of neutron activation. The amount of sample preparation required for flameless atomic absorption is often less than that required for flame atomization. Since tellurium had not been previously investigated by this technique, a thorough examination was undertaken on the feasibility of using the graphite furnace for routine geochemical analyses of this element. The use of the graphite furnace for trace metal analyses has been described by

Manning and Fernandez (6, 7).

EXPERIMENTAL

Apparatus. Absorption measurements were made with Perkin-Elmer models 403 and 503 atomic absorption spectrophotometers, equipped with the HGA-2000 graphite furnace, deuterium arc background corrector, Perkin-Elmer model 56 recorder, and a Perkin-Elmer "Intensitron" Te hollow cathode lamp. Nitrogen was used for the furnace purge gas. Microliter quantities of solutions were measured with 20λ, 50λ, and 100λ Eppendorf pipets. Sample decompositions were performed in teflon beakers.

Reagents. A stock solution containing 100 μg Te per ml was prepared by dissolving, with minimum heating, 100 mg of pure Te metal in about 5 ml of concentrated HNO_3 and 1 ml of concentrated HCl and diluting to 1 liter with deionized water. Standard Te solutions containing 1.00 μg/ml, 0.10 μg/ml, and 0.01 μg/ml were prepared by making appropriate dilutions of the stock with deionized water. Concentrated hydrofluoric acid was used for rock decomposition.

Procedure. Rock samples were pulverized, ground and sieved through an 80-mesh screen. Depending on the Te content of the sample, from 0.25 g to 1.25 g of the ground rock were weighed into a teflon beaker, and 1 ml of aqua regia was carefully added and thoroughly mixed with the sample. Fifteen ml of concentrated HF was added, and the mixture was taken to dryness on a hot plate at 100-110°C. After the residue was rewetted with 0.5 ml aqua regia, the HF treatment and evaporation were repeated. Then, 25 ml of 6 M HCl were pipeted onto the dried sample, and the mixture was stirred to dissolve all soluble material.

Three 5.00 ml aliquots of a sample solution prepared by the above method were pipeted into small glass vials and standard additions of 50λ and 100λ of a 0.1 μg/ml Te standard were made to two of the vials. One ml of methyl isobutyl ketone (MIBK) was pipeted into each of the three vials, and the Te was extracted by gentle shaking of the capped vials for 2 minutes. A 50λ aliquot of the organic extract was pipeted into the grooved tube of the graphite furnace, where it was dried for 30 seconds, charred for 60 seconds and atomized for 10 seconds at settings of 80, 350 and 1800, respectively, on the HGA-2000 power supply. Peak absorbances were measured at 214.3 nm with a spectral band width of 0.2 nm and a recorder full scale range of 0.25 absorbance units. The response was plotted against added Te, and the Te content of the sample was determined by the usual standard additions method.

RESULTS AND DISCUSSION

Sample Preparation. For a total analysis of trace elements in geological materials, either a fusion or HF digestion must be utilized for sample decomposition. The high salt concentrations resulting from a fusion make this approach undesirable when atomic absorption is to be used for analysis, so the HF procedure was selected. Preliminary sample digestions were carried out in a sealed teflon vessel to prevent the loss of volatiles during decomposition. A later investigation into the feasibility of using open teflon beakers for the decomposition showed comparable signals from Te for a sample prepared either in an open or a closed system. Open beakers were subsequently used for sample decomposition.

Direct analysis of the acidic solution proved impossible, due to extremely heavy "smoke" at atomization. The well known extraction of Te from HCl solution into MIBK was utilized to separate the Te from the bulk of the sample, and thereby eliminate most of the smoke-producing contaminates. A previous report (5) indicated that this extraction is not very specific, and the presence of several foreign species suppresses the efficency of the Te extraction. The use of standard additions prior to the extraction, however, compensates for varying extraction efficiencies. Recovery of Te spikes extracted from samples, based on sensitivity comparisons to extracted standards, ranged from 33% to 100%.

Furnace Parameters. The performance of the graphite furnace for Te determination was investigated using both standard and grooved graphite tubes. Figures 1 and 2 show the peak response for Te for the standard and grooved tubes as a function of atomization and charring temperature. The charring and atomization temperature selected for the standard tube on the basis of these data were $600^{\circ}C$ and $2000^{\circ}C$, respectively. When the grooved tube was in use, charring was done at

350 and atomization at 1800. It should be noted that the temperature stated above for the grooved tube are those indicated on the HGA-2000 power supply, which do not correspond to °C, as the grooved tube has a different resistance from the standard tube.

The reproducibility of Te signals obtained from the graphite furnaces is presented in Table I. The measurements were made in the "Peak Read" mode on a Perkin-Elmer model 503 atomic absorption spectrophotometer, with the first reading arbitrarily set at 1000. The degradation in precision, when the grooved tube is used for Te in MIBK, undoubtedly reflects the increased difficulty in pipeting organic solutions with Eppendorf pipets. No values are shown for extracted Te in the standard tube due to very poor precision. This is attributed to spreading of the organic solvent in the tube before drying. The depression in the grooved tube restrains the sample to the center of the tube, improving reproducibility. Therefore, the grooved tube was used for the analyses.

The atomic absorption sensitivity for Te when using the furnace without purge gas interruption, was 125 pg for 1% absorption with the standard tube and slightly poorer with the grooved tube. Utilizing automatic purge gas interruption during atomization, the sensitivity increased considerably, with 30 pg of Te giving a 1% peak absorption for both tubes. Automatic gas interrupt was used for the analyses.

The absolute detection limit for Te standards extracted into MIBK and run at the established conditions for the grooved tube was about 70 pg. This limit was seldom realized, however, for actual sample analysis, due to an increased noise level at atomization, arising from dense smoke. The poorest detection limit encountered on an actual sample was 200 pg.

Results. A series of 20 rock samples, including 6 USGS standards, were run by the above method. A discussion of the geological significance of the data gathered is being published separately. Table II presents results for a few of the rocks analyzed. No previously existing Te data on the USGS standards is available for comparison.

In order to establish the validity of the analyses, a known amount of Te was added to a weighed portion of one of the analyzed rock samples, which was then decomposed and analyzed by the procedure described. The sample Te was subtracted from the total Te found to determine the recovery. As seen in Table III, the recovered Te agreed well with the amount added.

ACKNOWLEDGMENT

The author is grateful to Dr. O. K. Manuel for his support and interest in this work.

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Figure 1. Peak response for varying atomization (A) and charring (B) temperatures using the standard graphite tube. Atomization at 2000°C for curve (B).

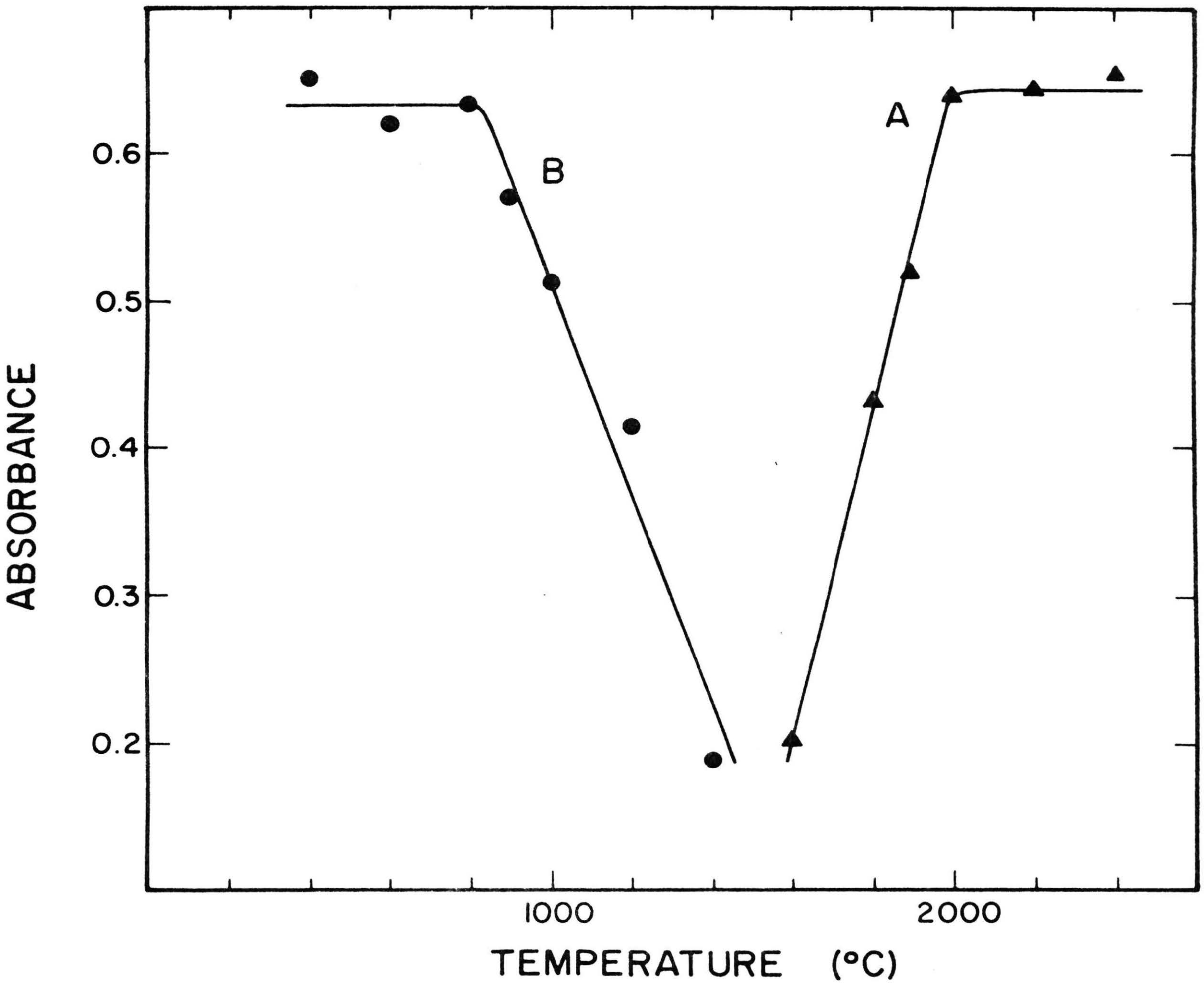

Figure 1

Figure 2. Peak response for varying atomization (A) and charring (B) temperatures using the grooved graphite tube. Atomization at 1800°C for curve (B).

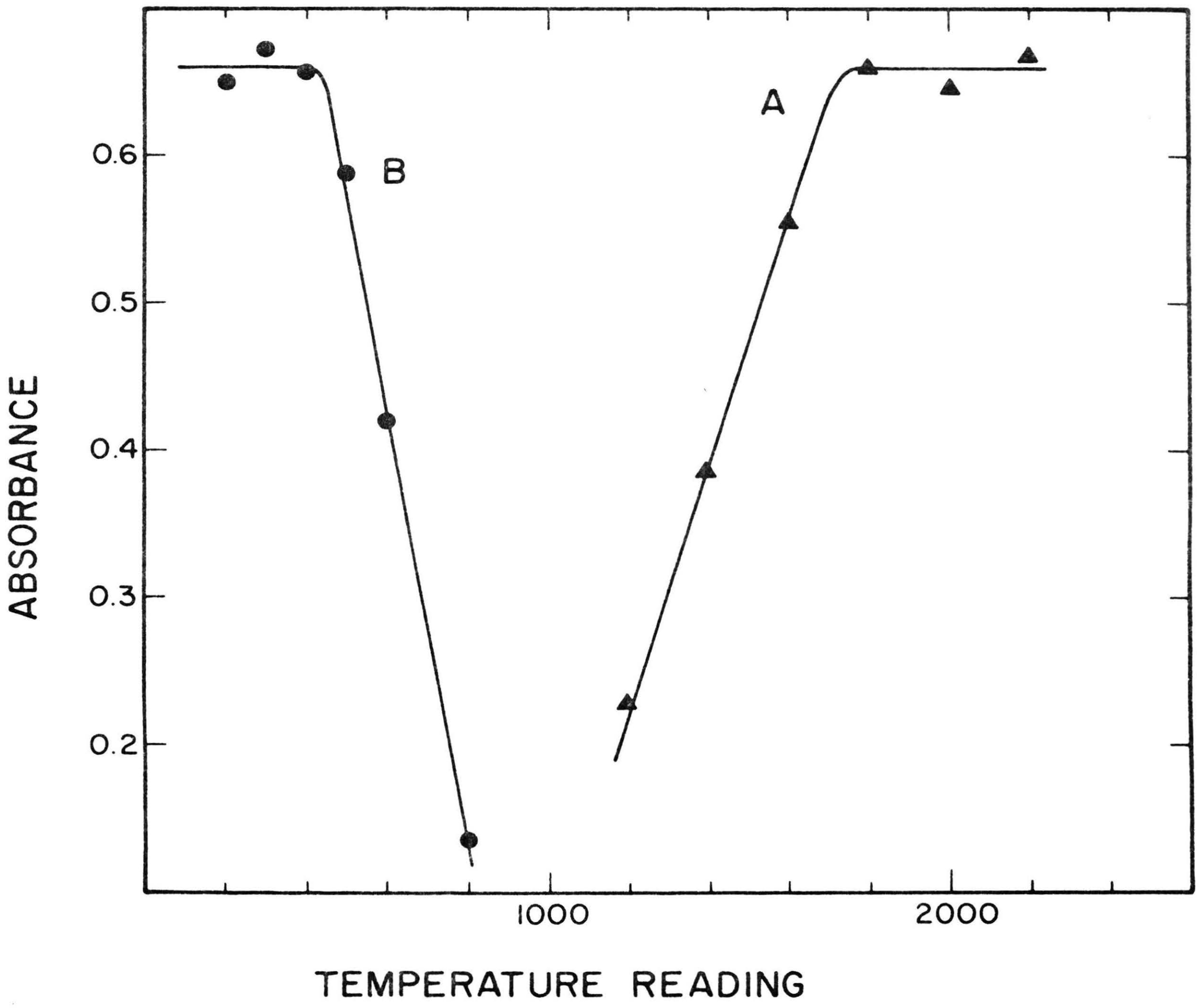
ABSORBANCE
0.6
0.5
0.4
0.3
0.2
B
A
1000
2000
TEMPERATURE READING

Table I. Precision of Measurement

Graphite Tube	Solvent	Nanograms Te	No. of Measurements	Range of Readings	Average Reading	Standard Deviation	Relative Std. Dev.
Standard	Water	5	10	1000-1029	1013	9.71	0.96%
Grooved	Water	5	10	998-1074	1039	28.5	2.74%
Grooved	MIBK	5	10	926-1096	1005	70.1	6.97%

Table II. Te in Rocks

Samples	Number Analyzed	ppb Te
Igneous Rocks		
Hornblende Basalt (Chaffee County, Colo.)	2	154 ± 11
Olivine Gabbro (Wichita Mts., Okla.)	2	58 ± 7
Andesite (USGS Standard AGV-1)	1	$< 16^a$
Granodiorite (USGS Standard GSP-1)	3	20 ± 3
Graphic Granite (USGS Standard G-2)	1	$< 3.4^a$
Sedimentary Rocks		
Dolomitic Limestone (Rochester, N.Y.)	5	1009 ± 44
Calcereous Shale (Lima, N.Y.)	2	42 ± 5
Red Sandstone (Potsdam, N.Y.)	2	28 ± 6

[a] Detection Limit

Table III. Te Recovery from Dolomitic Limestone

Tellurium	Amount
Present in Sample	254 ng
Added	100 ng
Recovered	358 ng
Net Recovered	104 ng
Recovery	104%

IV. TELLURIUM IN ROCKS

by

Richard D. Beaty

Manuscript as submitted to _Chemical Geology_ (1973).

ABSTRACT

Twenty different rocks have been analyzed for tellurium by atomic absorption. The average tellurium content of 12 igneous rocks is 82 ppb, with a range, 3.4 ppb $\geq$ Te = 210 ppb. In ultrabasic rocks, the tellurium content is < 10 ppb. Of the rocks analyzed, carbonates showed the highest Te content, 1-2 ppm, and the tellurium concentrations in 6 sedimentary rocks decrease in the following order: carbonates > shales > sandstones.

INTRODUCTION

Data on the distribution of tellurium in the Earth's crust are virtually nonexistent (Rankama and Sahama, 1950; Turekian and Wedepohl, 1961; Goldschmidt, 1958; Horn and Adams, 1966). The available data are generally limited to areas of tellurium mineral deposits, except for early reports on the pioneering work by the Noddacks (1930, 1931, 1936).

Noddack and Noddack (1931) reported an average of 2 ppm tellurium in primary magmatic sulfides, and Noddack (1936) found a similar tellurium content for shales. Sindeeva (1964) presents one of the more comprehensive reports on the mineralogy and geochemistry of tellurium but she was unable to detect tellurium in any of the major rock types. Everett (1964) analyzed for tellurium near the mining areas of Arizona, Colorado, New Mexico and Utah, but his results are limited to tellurium concentrations above 10 ppm. Horn and Adams (1966) note that the sulfur and selenium contents in sedimentary-oceanic materials are too high to be accounted for by weathering of igneous rocks, and they suggest that a significant part of these elements in sedimentary and oceanic domains was derived from a volcanic source. The behavior of tellurium was not considered in this geochemical material balance, due to the absence of abundance data.

In addition to providing data for a better understanding of the geochemistry of tellurium, this study was undertaken as a preliminary step in our attempt to understand man's role in altering the natural distribution of this toxic element in the environment. In an earlier report (Beaty 1973a), we noted that atomic absorption could be used to determine tellurium in the parts per billion (ppb) range in sulfide ores, but a relatively high reagent blank and matrix problems resulting from the decomposition process for siliceous materials severely limited the application of this method to general geochemical work. This procedure has been modified to take advantage of flameless sampling devices described by Manning and Fernandez (1970) and Fernandez and Manning (1971).

The data presented in this paper result from a method developed for the determination of sub-nanogram quantities of tellurium in rocks utilizing the Perkin-Elmer HGA-2000 graphite furnace. A summary of the technique follows. A detailed description of the method is being published separately (Beaty, 1973b).

PROCEDURE

Rock samples were pulverized, ground and sieved to -80 mesh size. A 1.25 g portion of the ground sample was weighed into a teflon beaker, 1 ml of aqua regia (3 HNO_3:1 HCl) was added, the beaker swirled to throughly wet the sample, and 15 ml of concentrated HF was then added. This mixture was taken to dryness on a hot plate at 100-110°C, the residue rewetted with 0.5 ml aqua regia, 10 ml of concentrated HF added, and the solution again taken to dryness. Then 25 ml of 6 M HCl were pipetted onto the dried sample, and the mixture was stirred to dissolve all soluble material.

Sample solutions prepared by the above method were analyzed by the standard additions technique. Three 5.00 ml aliquots of the sample solution were pipetted into small glass vials. A standard tellurium solution (0.1 γ/ml) was added to two of the vials. Eppendorf pipettes were used to add 50λ of the standard solution to one vial and 100λ to another, i.e., the amounts of Te added to the three vials were 0, 5 and 10 nanograms, respectively. One ml of methyl isobutyl ketone was then pipetted into each vial, and the tellurium was extracted by gentle shaking of the capped vials for 2 minutes. A 50λ aliquot of the organic phase was pipetted into the grooved graphite tube of the atomizer, where it was dried, charred for 30 seconds at $\approx$ 600°C and tellurium atomized at $\approx$ 2000°C.

Absorption measurements were made on a Perkin-Elmer model 403 atomic absorption spectrophotometer equipped with the HGA-2000 graphite furnace, deuterium background corrector, Perkin-Elmer model 56 recorder, and a Perkin-Elmer "Intensitron" Te hollow cathode lamp.

RESULTS AND DISCUSSION

The results obtained from this study are shown in Table 1. The samples included six USGS standard rocks which had been analyzed earlier for the two lighter chemical analogs of tellurium, selenium (Sen Gupta, 1968; Flanagan, 1969) and sulfur (Brunfelt and Steinnes, 1967). The expected concentrations of tellurium in these six rocks were calculated from their sulfur and selenium contents and from the atomic ratios, S/Te and Se/Te, reported for the cosmic abundances of the elements (Suess and Urey, 1956). The concentrations of tellurium determined in these six rocks agree with the concentrations calculated in this manner, except that the tellurium content of the basalt, BCR-1, could not be measured due to excessive background interference.

Due to the limited number of samples analyzed in this study, our results provide no detailed information on the geochemical distribution of tellurium. However, in view of the paucity of other data on the tellurium content of rocks, a few comments on our results seem appropriate.

The average tellurium content of the igneous rocks analyzed, 82 ppb, agrees with the estimate by Noddack and Noddack (1930), but the tellurium content of these rocks is higher than the estimate by

Vinogradov (1956). Sindeeva (1964) was unable to detect tellurium in igneous rocks of the Soviet Union and concluded that their tellurium content was less than 100 ppb. However, her analyses indicated that the average selenium content of these rocks was nearer to the estimate by the Noddacks (1930), and about 10 times higher than the estimate by Vinogradov (1956). The tellurium content of igneous rocks analyzed in this study vary by almost two orders of magnitude, but additional analyses will be required to define the distribution of tellurium in the different types of igneous rocks.

No tellurium was detected in ultrabasic rocks, but the upper limits established for the two samples suggest that the tellurium content of ultrabasic rocks is likely to be lower than that of igneous or sedimentary rocks. This distribution of tellurium would agree with the trend observed for selenium in rocks from the Soviet Union (Sindeeva, 1964).

The highest concentrations of tellurium were observed in sedimentary rocks. The distribution of tellurium in sedimentary rocks appears to parallel that observed for chlorine and bromine (Horn and Adams, 1966) and iodine (Becker *et al.*, 1972). The high tellurium content in argillaceous material may result from the adsorption of tellurium on fine grained material. Although our results do not indicate the mechanism responsible for the distribution of tellurium in sedimentary rocks, the apparently similar distribution of tellurium and the heavy halides is intriguing in view of the correlation between iodine and tellurium in stony meteorites where the concentrations of each element vary over two orders of magnitude (Pelly and Lipschutz, 1971).

Obviously, a more detailed study on the natural distribution of tellurium in the Earth's crust is needed. Tellurium may be redistributed in the environment through burning of low-grade, sulfur-rich coals and through the reprocessing of sulfide ores for more economically important elements. Since tellurium is highly toxic to mammals (Bowen, 1966), information on its distribution as a waste product is also needed.

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We are grateful to Dr. W. T. Schrenk, Emeritus Professor of Chemical Engineering at the University of Missouri-Rolla, for his advice and encouragement during the course of this investigation. The assistance of Mr. V. J. Becker with the literature survey and with helpful comments on the manuscript is deeply appreciated.

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Table 1

Tellurium in Rocks

Samples	Source	Number of Samples Analyzed	Te (ppb) Observed	Te (ppb) Expected	S (ppm) Sen Gupta (1968)	Se (ppb) Brunfelt and Steinnes (1967)
Ultrabasic Rocks						
Peridotite (USGS Standard PCC-1)	USGS	1	< 8	3-5	100	22
Dunite (USGS Standard DTS-1)	USGS	1	< 15	0.5-5	100	4
Igneous Rocks						
Basalt (USGS Standard BCR-1)	USGS	1	*	12-26	500	103
Basalt (Lintz, Rhenish Prussia)	Wards†	1	88			
Hornblende Basalt (Chaffee County, Colo.)	Wards	2	154 ± 11			
Olivine Gabbro (Wichita Mts., Okla.)	Wards	2	58 ± 7			
Hypersthene Grabbro (Glamorgen Tp., Ontario)	Wards	2	70 ± 4			
Olivine Syntite (Butte, Mont.)	Wards	2	82 ± 4			
Syntite (Wausau, Wisc.)	Wards	2	74 ± 4			
Andesite (USGS Standard AGV-1)	USGS	1	< 16	0.9-5	100	8
Granodiorite (USGS Standard GSP-1)	USGS	3	20 ± 3	7-26	500	59
Biotite Granite (Barre, Vermont)	Wards	2	210 ± 21			
Graphic Granite (Auburn, Maine)	Wards	2	132 ± 20			
Granite (USGS Standard G-2)	USGS	1	< 3.4	0.6-10	200	5
Sedimentary Rocks						
Limestone						
Dolomitic (Rochester, N.Y.)	Wards	5	1009 ± 44			
Argillaceous (Trenton Falls, N.Y.)	Wards	2	1726 ± 8			
Shales						
Calcereous (Lima, N.Y.)	Wards	2	42 ± 5			
Argillaceous (Rochester, N.Y.)	Wards	2	789 ± 3			
Sandstone						
Red (Potsdam, N.Y.)	Wards	2	28 ± 6			
White (Klondike, Mo.)	Wards	1	< 6			

*Excessive background interference prevented determination.

†Wards Natural Science Establishment, Inc., Rochester, N.Y., U.S.A.

VITA

Richard Duane Beaty was born on March 5, 1945 in West Frankfort, Illinois. He received his primary and secondary education in Centralia, Illinois. He attended the University of Illinois from 1963 to 1966 and the University of Missouri-Rolla from 1966-1967, where he received his Bachelor of Science degree in chemistry in May, 1967. In 1965, he married Danya Lynn Gillespie. They now have two children, a son, Jeffrey, and a daughter, Shannon.

He entered Graduate School at the University of Missouri-Rolla in 1969 as a NDEA research fellow and teaching assistant in the Chemistry Department. He received his Master of Science degree in chemistry in 1971 and has since been pursuing the degree of Doctor of Philosophy.