

## DETERMINATION OF TELLURIUM IN GEOCHEMICAL MATERIALS BY FLAMELESS ATOMIC-ABSORPTION SPECTROSCOPY

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**Summary**—A method is described for the determination of tellurium at nanogram levels in rocks and in other complex materials by the use of flameless atomic-absorption spectroscopy. A very selective organic extraction procedure is applied to avoid matrix interference effects during extraction of Te and the atomization stage in the graphite furnace. Prior separation of iron and other interfering elements is achieved by a combined cupferron-ethyl acetate extraction. Tellurium is extracted from 6M hydrochloric acid with MIBK and stripped into aqueous medium. Pipetting of the aqueous extract into the graphite furnace gives fairly good instrumental reproducibility (2–3% error). Detection limits of about 10 ppM Te for a 0.5-g sample have been achieved with the medium-performance apparatus used. Results for Te in some geochemical reference materials are reported. Indications are given for the determination of Sb and Mo in the same solutions.

Until very recently data on the distribution of tellurium in non-mineralized silicate rocks have been practically non-existent. The 1973 tables of elemental abundances in geological materials<sup>1</sup> reported for tellurium only the upper abundance limit (<1 ppm) for a limited number of samples. The lack of data on Te abundances accounted essentially for the difficulties in developing a method to determine this element at nanogram levels in materials with a very complex matrix such as silicate rocks. In recent years more sophisticated techniques such as neutron activation,<sup>2</sup> isotope-dilution mass spectrometry<sup>3</sup> and atomic-absorption spectroscopy (AAS) have been employed to analyse geological materials for Te. With this last technique Te has been detected at nanogram levels by using the sampling-boat system<sup>4</sup> and the graphite furnace.<sup>5</sup> The recently introduced hydride system may undoubtedly give a valuable improvement in analysis for Te in rocks because of its simplicity and sensitivity. Nevertheless, the graphite furnace has the unique advantage that the same test solutions can be used for determining other trace elements. This paper describes a stepwise chemical separation method for Te from silicate matrices and subsequent analysis for Te by use of a heated graphite atomizer. Included are some data regarding the determination of Sb and Mo in the same analytical solution.

### General analytical comments

The major difficulty in the determination of Te and, in general, of trace elements in rock samples by use of the graphite furnace is the necessity for separation of these elements from the major elements constituting the silicate matrix. If this is not done, the analysis may be affected by errors that even apparently adequate procedures such as standard-addition methods cannot minimize. Tellurium is usually separated from other elements by organic solvent techniques. The extraction from fairly concentrated hydrochloric acid medium is easy,<sup>6</sup> but not very specific and many other elements follow Te into the organic phase.

On the one hand this may affect the efficiency of the Te extraction and on the other lead to high background absorption during subsequent atomization in the graphite furnace. Of the elements extracted together with Te from 6M hydrochloric acid, iron is by far the most important since it is almost totally extracted and is usually a major constituent in geological materials. None of the other co-extracted elements<sup>6</sup> is normally present in rocks in sufficient amount to cause interference. A previously reported procedure for determination of Te in rocks, based on a simple extraction with MIBK (methyl isobutyl ketone) and use of a standard-addition method<sup>5</sup> was found not of general application because of matrix interference effects. Our initial attempts at directly pipetting the MIBK extract into the furnace were unsuccessful in most cases, because of high background absorption exceeding the background-correction capabilities of the instrument used. This difficulty may be overcome only by using a very selective extraction procedure for tellurium.

### Separation of tellurium from interfering elements

As iron is the only element which may seriously affect the efficiency of Te extraction by MIBK, its interference effects were investigated by double extraction of 5-ppM Te solutions containing various amounts of iron. Tellurium recovery in the first and second MIBK extracts is shown in Fig. 1 (the absorption was measured after complete chemical treatment as reported below). Removal of Te into the MIBK phase in the first extraction decreases strongly with increasing Fe content but increases in the second extraction. This means, of course, that the presence of large amounts of iron (above ~400 ppm) inhibits extensive extraction of Te by MIBK and that this last becomes effective only if most of the iron is previously extracted. Many highly efficient iron extractants are known but in our case a supplementary condition is the non-removal of tellurium. After a series of experiments with various extractants a cupferron-ethyl acetate extraction was found to give the best selective removal of iron from hydrochloric acid media containing Te, as shown by B in Fig. 1. Recovery of Te was >80% and independent of the original iron concentration.

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It is well known that the reproducibility of absorption signals obtained by use of the graphite furnace is a function of the medium used, and is often poorer for organic than for aqueous solutions. There may be several reasons for this, such as the increased difficulty in pipetting organic solutions, or spreading or irregular absorption of the organic solvent in the tube before drying. For this reason aqueous solutions are, when possible, preferred. Tellurium present as the chloride complex in the MIBK phase is easily stripped into an aqueous phase with  $<0.8M$  hydrochloric acid concentration. As the stripping is also effective with high organic-aqueous volume ratios, very small final volumes of analytical solutions can be used, thus increasing the analytical sensitivity. A working curve obtained by pipetting constant volumes ( $20 \mu\text{l}$ ) of  $0.5\text{--}10 \text{ ppM}$  Te solutions (after the complete extraction cycle) was found to be linear. We recommend the pipetting of constant volumes of solution to avoid any error inherent in possible dispersion of solution along the tube.

As tellurium may be partially lost before the atomization stage a matrix modification technique<sup>7-10</sup> was tried, nickel being added to the analytical solution after the complete extraction cycle, but without much improvement. This suggests that at the charring temperature used loss of Te by volatilization does not occur. Besides Fe and Te, many other metals are extracted by cupferron-ethyl acetate<sup>11,12</sup> and MIBK,<sup>9</sup> including the geochemically important trace elements Au, Tl, Ge, Sb, Mo, As, Pt which are thus potentially determinable in the solution used for the Te determination. Preliminary investigations on Mo and Sb were encouraging. Both are almost totally ( $>90\%$ ) extracted with cupferron-ethyl acetate and are easily stripped in the same way as Te. Procedures for determination of some of these elements will be reported elsewhere.

#### EXPERIMENTAL

##### Apparatus

A Perkin-Elmer Model 306 atomic-absorption spectrophotometer with a Model 56 recorder, a Perkin-Elmer Intensitron<sup>®</sup> tellurium lamp, and a Model HGA-2000 furnace equipped with a deuterium background corrector were used.

##### Operating conditions

###### Spectrophotometer

Wavelength	214.3 nm
Spectral band-width	0.2 nm
Scale expansion	1x

###### HGA module

Drying temperature	150°	15 sec
Charring temperature	600°	35 sec
Atomization temperature	2035°	12 sec
Argon flow	4 meter divisions, interrupted	
Sample volume	20 $\mu\text{l}$	

##### Reagents and standards

Tellurium certified atomic-absorption standard ( $1000 \mu\text{g/ml}$ ) was obtained commercially. Working standards ( $0.2, 0.51, 1, 5, 10 \text{ ng/ml}$ ) were prepared by diluting the concentrated standard with demineralized water. Super-pure concentrated reagent grade hydrofluoric, nitric and hydrochloric acids (Merck) were used.

##### Procedure

Weigh a  $0.5\text{-g}$  powdered sample into a  $50\text{-ml}$  Teflon vessel,<sup>13</sup> add  $1 \text{ ml}$  of *aqua regia* and swirl the vessel to wet the sample, then add  $10 \text{ ml}$  of concentrated hydrofluoric acid, evaporate to dryness on a hot-plate at  $100\text{--}110^\circ$ , add  $0.5 \text{ ml}$  of *aqua regia* and  $5 \text{ ml}$  of hydrofluoric acid to the residue and repeat the digestion. Dissolve the final residue in  $25 \text{ ml}$  of  $6M$  hydrochloric acid with magnetic stirring.

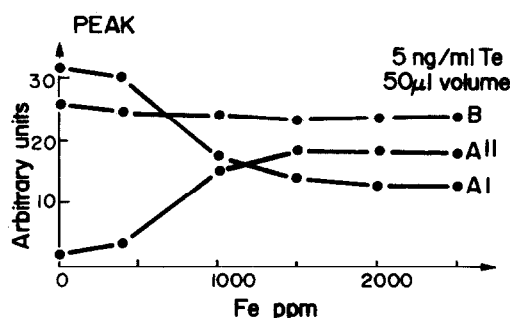


Fig. 1. Effects of varying amounts of iron on the extraction of Te by MIBK. AI and AII: Te recovered in the first and second extractions respectively. B: Te recovered after prior Fe extraction with cupferron-ethyl acetate. Peak height in arbitrary units.

Transfer the solution to a  $60\text{-ml}$  separatory funnel, add  $4 \text{ ml}$  of freshly prepared  $4\%$  cupferron solution and  $10 \text{ ml}$  of ethyl acetate and shake mechanically for  $1 \text{ min}$  (vigorously for  $3\text{--}4 \text{ min}$  if shaking manually). Transfer the aqueous layer into a beaker and discard the organic layer if analysis for other elements (Sb, Mo, etc.) is not required. Put the aqueous solution back in the funnel and complete the Fe extraction by shaking with  $5 \text{ ml}$  of ethyl acetate. Separate the aqueous layer and shake it for  $1 \text{ min}$  with  $4 \text{ ml}$  of MIBK. Transfer the MIBK phase into a  $10\text{-ml}$  borosilicate glass bottle and add  $1 \text{ ml}$  of demineralized water. Gentle shaking by hand is sufficient to concentrate the Te in the aqueous phase. Prepare standards by treating analogously  $25 \text{ ml}$  of the standard Te solutions. Pipette  $25 \mu\text{l}$  of the aqueous concentrate into the furnace and analyse under the conditions outlined above.

#### RESULTS

##### Sensitivity and reproducibility

A very low blank reading was obtained, even with large amounts of iron in the starting solution. A  $20\text{-}\mu\text{l}$  sample of  $0.2\text{-ppM}$  Te solution ( $40 \text{ pg}$  of Te) gave an absorption reading about twice that of the blank. This value represents the instrumental sensitivity limit for detection of Te and corresponds to a content of  $10 \text{ ppM}$  Te in the sample

Table 1. Tellurium in reference samples,  $\text{ng/g}$

Sample	Te found	Literature data*		
		A <sup>2</sup>	B <sup>3</sup>	C <sup>14</sup>
W-1	$<10$	$<90$	11	
G-2	$<10$	$<90$	5	3, 4
				AGV-1
				$<10$
	2	16		
GSP-1	32-36		31	20
BCR-1	15-25	$<90$	2	
PCC-1	$<10$		2	$<8$
DTS-1	$<10$		3	$<15$
Syenite 2	$<10$		2	
Sulphide	1200-1350		1490	
GA	$<10$			
GH	$<10$			
DR-N	12-15			
BR	10-11			
Fe biotite	12			
T-1	24-29		31	

\* A = neutron activation; B = mass spectrometry; C = flameless AAS.

when 0.5 g of sample is used. Instrumental precision was checked by means of a series of replicate readings on 1- and 10-ppM Te aqueous solutions. Good reproducibility (2-3% coefficient of variation) was found for both concentrations.

#### *Standard geological materials*

The method has been applied to the analysis of silicate standards for some of which tellurium data had been obtained by techniques such as neutron activation and isotope-dilution mass spectrometry. The results are reported in Table I. Our data agree sufficiently well with other data for samples which have relatively high Te contents. Unfortunately the Te contents of most of the standards are below the analytical sensitivity achieved with the medium-performance instrument used. A standard sulphide was analysed by dissolving the sample in *aqua regia* and the results are concordant with documented data (Table 1). The method seems to be suitable for microanalysis (1-10 mg of sample) of Te-rich materials such as ore minerals and lunar and meteoritic materials.

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