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Differential Determination of Tellurium(IV) and Tellurium(VI) by Atomic Absorption Spectrophotometry after Hydride Generation. Combined Use of Titanium(III) Chloride as a Prereductant and Sodium Borohydride Solution

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Sensitive determination of tellurium was investigated by atomic absorption spectrophotometry after hydride generation and differential determination of tellurium(IV) and tellurium(VI) in acidic solution was carried out. When sodium borohydride solution is used without any prereductant, only the signal from tellurium(IV) is obtained. On the other hand, when titanium(III) chloride solution is added before the addition of borohydride solution, total signal from tellurium(IV) and tellurium(VI) can be obtained; 30—60 s of prereduction is required. The effectiveness of the titanium(III) chloride–borohydride reduction system is shown in the interference study. The interference of selenium(IV) is eliminated up to 200 fold *vs.* 0.25 μg of tellurium(IV) in 20 cm^3 of 3 mol dm^{-3} hydrochloric acid by the use of 2 cm^3 of 5% w/v titanium(III) chloride solution as a prereductant. Tellurium in steel and sulfur (commercial reagent) can be determined satisfactorily without isolation of tellurium from matrix by this method. Detection limit of the method is 8 ng. The coefficient of variation of the method is 2.4% in the ten determinations of 0.25 μg of tellurium.

Determination of a trace amount of tellurium has become of interest in recent years. Tellurium is harmful to the strength of steel[1,2] and high temperature alloys[3] even in a low concentration; in geochemical aspects it is useful as an indicator element.[4–6] Bismuthiol-II is one of the most sensitive reagents in the spectrophotometric determination of tellurium(IV),[7–9] but complete separation of tellurium from interfering ions, *e.g.*, selenium, copper, vanadium, and palladium is required. Although flame atomic absorption spectrophotometry is especially convenient method for the determination of tellurium containing selenium,[10–12] the sensitivity is not yet sufficient for the determination of tellurium in concentration below ppm, and tellurium should be concentrated by solvent extraction[2,10] or coprecipitation with arsenic.[9,10] Hydride generation-atomic absorption spectrophotometry has also been applied to determine tellurium because of its high sensitivity.[13–15] In the method titanium(III) chloride together with magnesium[13] or sodium borohydride[14,15] has been used as a reductant to generate tellurium hydride. There have been no reports, however, on the differential determination of tellurium(IV) and tellurium(VI) in the same solution by atomic absorption spectrophotometry. In order to find suitable experimental conditions for determining tellurium by hydride generation-atomic absorption spectrophotometry, experiments have been carried out.

It was found that sodium borohydride reduces tellurium(IV) to tellurium hydride and is not effective for the reduction of tellurium(VI), and that titanium(III) chloride reduces tellurium(VI) to tellurium(0) *via* tellurium(IV). By utilizing the differences in ability of reduction for tellurium spieces, differential determination of tellurium(IV) and tellurium(VI) in the solution was satisfactorily carried out. When sodium borohydride solution was added alone to the mixed solution of tellurium(IV) and tellurium(VI), only the signal from tellurium(IV) was obtained and not from tellurium(VI). On the other hand, when titanium(III) chloride solution was added to the solution as a prereductant prior to the addition of borohydride solution, total signal from tetravalent and hexavalent tellurium was obtained. Both the concentration of titanium(III) chloride and the prereduction time affected the sensitivity of this method.

This procedure was applied to the determination of trace amounts of tellurium in steel and sulfur.

Experimental

Apparatus. A Hitach Model 170-50 type atomic absorption spectrophotometer with deuterium background corrector and a tellurium hollow-cathode lamp (Hamamatsu TV) were used. A modified Hitachi arsenic determination unit was used for the generation of tellurium hydride; a reaction vessel (vol 115 cm^3) was connected to a dispenser (REBURET, Nippon Garasu Ryoki Co., Ltd.) with a silicone tube ($\phi = 1.5$ mm) attached firmely to a teflon cap as shown in Fig. 1. A prescribed volume of borohydride solution was introduced

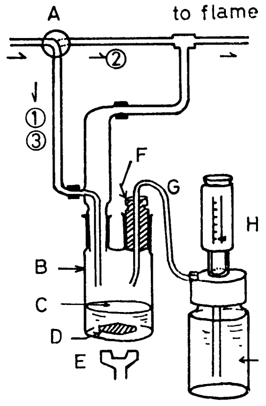

Fig. 1. Reaction vessel and piping diagram used for the evolution of tellurium hydride.

A: Electric valve, ①～③ flow paths of nitrogen; B: reaction vessel; C: sample solution; D: spin bar E: magnetic stirrer; F: Teflon cap; G: silicone tube; H: dispenser; I: sodium borohydride solution.

Table 1. Conditions for nitrogen-hydrogen flame

Wavelength		214.3 nm
Lamp current		4 mA
Slit width	inlet	0.4 mm
	outlet	0.5 mm
Nitrogen flow rate		8 dm^3 min^{-1}
Hydrogen flow rate		7 dm^3 min^{-1}
Aux. nitrogen flow rate		2.5 dm^3 min^{-1}
Height of beam above burner tip		20 mm

instantly from the dispenser into the reaction vessel through the silicone tube. Generated tellurium hydride was carried into a nitrogen-hydrogen flame (one slot burner with 10 cm) and atomic absorption signals were recorded with a Hitachi 056 type recorder. Conditions for the nitrogen-hydrogen flame are given in Table 1.

Reagents. Standard tellurium(IV) solution (1000 ppm Te(IV)-3 mol dm^{-3} hydrochloric acid): 2.000 g of metallic tellurium (99.999%) was dissolved in 8 cm^3 of nitric acid and 10 cm^3 of hydrochloric acid, and the solution was dried up on a water bath. Ten cm^3 of hydrochloric acid was added and the solution was dried up, the procedure being repeated three times. After addition of 500 cm^3 of hydrochloric acid, the solution was diluted exactly to 2000 cm^3 with water. The solution was used by sequential dilution. Standard tellurium-(VI) solution: 1.072 g of sodium tellurate ($Na_2TeO_4 \cdot 2H_2O$) was dissolved in hydrochloric acid and diluted exactly to 500 cm^3 with water (1000 ppm Te(VI)-3 mol dm^{-3} hydrochloric acid). The solution was also used by sequential dilution. Titanium chloride(III) solution (5% w/v): 12.5 g of titanium-(III) chloride was dissolved in 125 cm^3 of 6 mol dm^{-3} hydrochloric acid, and diluted to 250 cm^3. Sodium borohydride solution (5% w/v, 1% sodium hydroxide): Five grams of sodium borohydride was dissolved in 100 cm^3 of 1% w/v sodium hydroxide. Other reagents were of analytical reagent grade. Deionized water was twice distilled.

Procedure. Transfer a prescribed volume of sample solution containing less than 0.8 μg of tellurium into a reaction vessel, add 5 cm^3 of hydrochloric acid, and dilute the solution to 20 cm^3 with water. Put spin bar into the vessel and set up it on hydride generation unit. Pass nitrogen gas in the vessel for 20 s. Turn electric valve to pass nitrogen through bypass to burner, and start magnetic stirrer. Pour 5 cm^3 of 5% w/v borohydride solution into the vessel from a dispenser when stirring becomes stationary, and lead the generated tellurium hydride to burner with hydrogen generated at the same time and record the signal of tellurium on the recorder. Pass nitrogen through the vessel for cleaning when the signal returns to baseline. Then, exchange the reaction vessel for another one. Determination of one sample can be done within about 1 min.

Results and Discussion

For hydride generation-atomic absorption method, the geometry of reaction vessel, atomizer unit, flow rate of auxiliary nitrogen (or argon), volume and concentration of borohydride solution, volume of sample solution and its acidity play important roles in determining the detection limit and sensitivity. These factors were studied independently in order to elucidate individual effects.

Effect of the Concentration of Sodium Borohydride Solution. Effects of sodium borohydride solution in the concentration range 3—8% w/v and of the solution volume on the sensitivity were examined in 3 mol dm^{-3} hydrochloric acid. The use of low concentration of borohydride resulted in low sensitivity of the method and the solution of high concentration was less stable than that of low concentration. Increase of the volume of borohydride solution up to 8 cm^3 increased sensitivity of the method. On the other hand, the accuracy of the method decreased apparently when more than 5 cm^3 of borohydride was used. Because of these limitations, 5 cm^3 of 5% w/v sodium borohydride was used throughout this study in view of sensitivity and accuracy of the method.

Flow Rate of the Auxiliary Nitrogen. The flow rate of auxiliary nitrogen, which was made to flow through the reaction vessel, was chosen to be 0—5 dm^3 min^{-1}. With increase of the flow rate of nitrogen, the peak height of tellurium decreased gradually. Therefore, nitrogen was made to flow through a bypass after the removal of oxygen from the system. No significant difference in sensitivity appeared between nitrogen-hydrogen flame and argon-hydrogen flame.

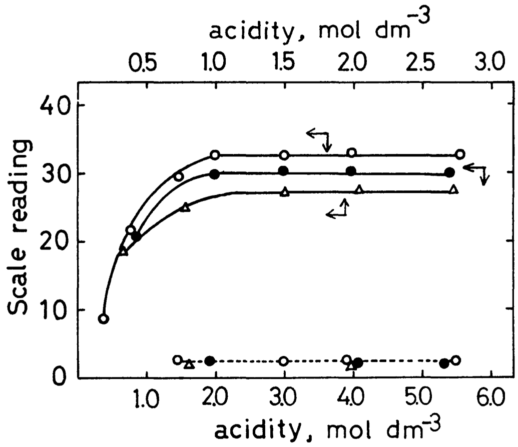

Fig. 2. Effect of acids on the sensitivity.
Te(IV): 0.25 μg/20 cm^3; 5% w/v $NaBH_4$: 5 cm^3.
-○- HCl, -●- HNO_3, -△- H_2SO_4.
Broken line indicates blank values for acids.

Effect of Acid. The sensitivity of this method was examined with use of a borohydride solution in hydrochloric acid, nitric acid, or sulfuric acid. The results are shown in Fig. 2. The absorption peaks of tellurium are slightly less in the cases of nitric acid and sulfuric acid media than in the case of hydrochloric acid medium, but in each case constant signals were obtained in the acid concentration range 2—5.5 mol dm^{-3}.

When the reaction vessel was replaced by a small one (vol 50 cm^3), the difference in peak height decreased, almost the same signal being obtained in hydrochloric acid and nitric acid media.

Volume of Solution in the Reaction Vessel. The efficiency of the reduction of tellurium(IV) to tellurium hydride decreased almost linearly with increase of the volume of solution in the reaction vessel from 10 to 50 cm^3; *e.g.*, the peak height of 0.25 μg of tellurium in 50 cm^3 was about one fourth of that in 10 cm^3. Therefore the volume of sample solution was chosen to be 20 cm^3 in order to attain best detection limit and precision of the method.

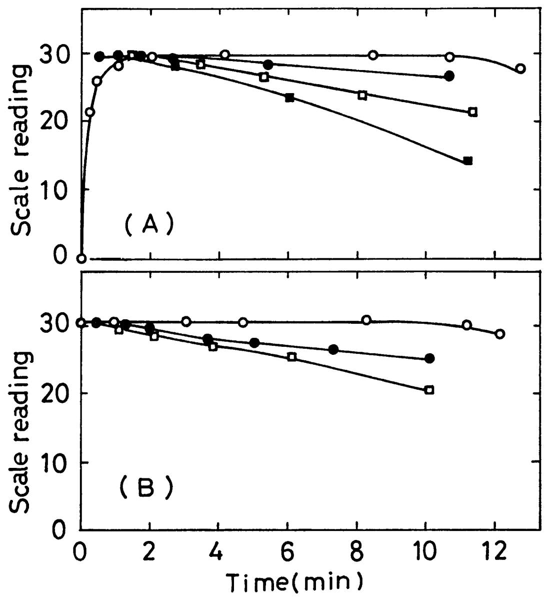

Fig. 3. Effect of the amount of titanium(III) chloride as a function of prereduction time.
(A) Te(VI), 0.25 μg/3 mol dm^{-3} HCl, (B) Te(IV), 0.25 μg/3 mol dm^{-3} HCl. 5% w/v $NaBH_4$: 5 cm^3, 5% w/v $TiCl_3$: -○- 1 cm^3, -●- 2 cm^3, -□- 4 cm^3, -■-5 cm^3.

Addition of Titanium(III) Chloride as a Prereductant of Tellurium(VI). Tellurium(VI) could not be reduced to tellurium hydride with borohydride alone (Fig. 3). Reduction of tellurium(VI) was carried out satisfactorily by the use of titanium(III) chloride together with borohydride. However, the peak height changes apparently with the concentration of titanium chloride(III) and prereduction time. In order to attain constant reduction of tellurium(VI) to tellurium(IV), the concentration of titanium(III) chloride and prereduction time, time from addition of the reagent to the injection of borohydride solution, were examined. The results are shown in Fig. 3. More than 120 s of prereduction time is required to obtain constant peak height when 1 cm^3 of 5% w/v titanium(III) chloride is used. When 2 cm^3 of 5% w/v titanium(III) chloride is used together with borohydride, almost constant peak height is obtained within 20—120 s of prereduction time. The peak height of tellurium is reduced considerably with increase in the volume of titanium(III) chloride and the prereduction time. This suggests that tellurium(VI) is reduced gradually to tellurium(0) *via* tellurium(IV) by titanium(III) chloride and precipitates in the reaction vessel. The same phenomenon is observed for tellurium(IV) as shown in Fig. 3. Within 90 s of prereduction time, addition of 2 cm^3 of 5% w/v titanium(III) chloride to the acidic tellurium(IV) solution before addition of borohydride solution does not reduce the peak height and gives satisfactory result.

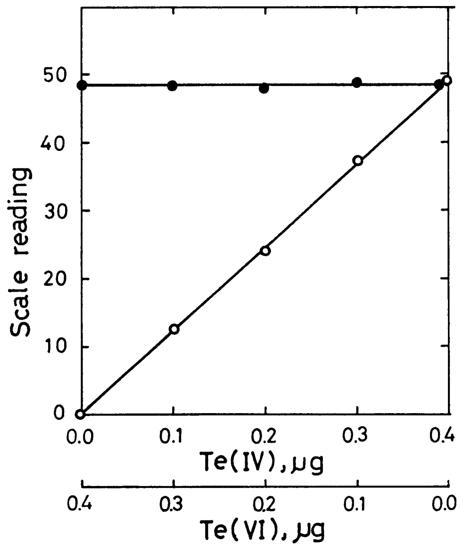

Fig. 4. Differential determination of tellurium(IV) and tellurium(VI).
Total tellurium: 0.4 μg; -○- 5% w/v $NaBH_4$: 5 cm^3, -●- 5% w/v $TiCl_3$: 2 cm^3 (prereduction time: 1 min), 5% w/v $NaBH_4$: 5 cm^3.

Differential Determination of Tellurium(IV) and Tellurium(VI). Figure 3 suggested the possibility of differential determination of tellurium(IV) and tellurium(VI). Tellurium(IV) was determined by reduction with borohydride alone, and total amount of tellurium was determined by the reduction of tellurium using 2 cm^3 of 5% w/v titanium(III) chloride for one min, followed by addition of 5% w/v sodium borohydride. The results are shown in Fig. 4, in which total amount of tellurium is kept 0.4 μg and the mixing degree of tellurium(IV) and tellurium(VI) is varied. Tellurium(IV) can be determined regardless of tellurium(VI) by borohydride alone as a reductant.

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Table 2. Comparison of permissible amounts of foreign ions for tellurium determination (within 10% negative error, ion (μg) *vs.* 0.25 μg of Te(IV))

Ion	Reduction system			
	$NaBH_4$$^{a)}$	KI–$NaBH_4$$^{b)}$	$TiCl_3$–$NaBH_4$$^{c)}$	$TiCl_3$–Mg$^{d)}$
Ag(I)	1.0	5.0	1.25	6.25
As(III)	0.75	2.5	5.0	7.5
As(V)	25	15	75	7.5
Bi(III)	5.0	5.0	3.75	50
Cu(II)	25	75	25	27.5
Hg(II)	1.25	1.25	2.5	1.25
Se(IV)	5.0	75	50	35
Sb(III)	5.0	5.0	5.0	7.5
Ni(II)	25	25	25	50
Co(II)	50	250$^{e)}$	250$^{e)}$	50
Pb(II)	125	250$^{e)}$	250$^{e)}$	125
Cd(II)	50	250$^{e)}$	200	250$^{e)}$

a) The following ions does not influence in excess amount (2500 μg): Na, K, Mg, Ca, Sr, Ba, Zn(II), Cr(III), Al(III), Fe(III), Mo(VI), Mn(II), V(V), SO_4^{2-}, NO_3^-, $C_2O_4^{2-}$, Br^-, SiO_3^{2-}, CH_3COO^-, ClO_4^-; Te(IV) 0.25 μg/3 mol dm^{-3}-HCl, 20 cm^3; 5% w/v $NaBH_4$, 5 cm^3. b) 20% KI, 1 cm^3, prereduction: 5 min. c) 5% w/v $TiCl_3$, 2 cm^3. d) 5% $TiCl_3$, 1 cm^3+0.5 g Mg, 6 mol dm^{-3} HCl. e) No influence.

ions on the determination of tellurium(IV) is given in Table 2. When borohydride alone is used as a reductant, relatively large interference arises in the order: arsenic(III)>silver(I)>mercury(II)>bismuth(III)>selenium(IV), antimony(III)>arsenic(V), copper(II), and nickel(II). Various reductants were used together with borohydride in order to eliminate the interference. Tin(II) chloride cannot be used because of uncorrectable background absorption. Potassium iodide is useful for eliminating the interference of some coexisting ions, especially selenium(IV); coexisting 200 fold of selenium(IV) *vs*. tellurium(IV) does not interfere when 2 cm^3 of 20% w/v potassium iodide is used as a prereductant (5 min of prereduction time). Titanium(III) chloride is also useful for eliminating the interference of selenium(IV) (Table 2).

Titanium(III) chloride–magnesium system[13] was also reexamined as regards the generation of tellurium hydride, and the results were compared with that of titanium(III) chloride–borohydride reduction system. Granular magnesium, wrapped in a wafer sheet, was added to sample solution containing titanium(III) chloride (6 mol dm^{-3} hydrochloric acid). The effect of diverse ions on the determination of tellurium is almost the same in these two reduction systems. However, reduction of tellurium by borohydride is superior to titanium(III) chloride–magnesium system in sensitivity, reproducibility, and handling.

In each reduction system, anions listed in Table 2 do not interfere in 10000 fold excess of tellurium in the determination.

Detection Limit and Precision of the Method. Calibration curves for tellurium(IV) determination by borohydride reduction and for tellurium(VI) by titanium(III) chloride–borohydride reduction are both linear up to 0.8 μg of tellurium. The coefficients of variation in the determinations of 0.25 μg tellurium(IV) and the same amount of tellurium(VI) were 2.4% and 2.9%, respectively. Detection limit of the method is 8 ng (S/N=2).

Determination of Tellurium in Steel. Prior to application of the method, the effect of iron(III) matrix on the determination of tellurium was examined (Fig. 5). Iron(III) does not interfere up to 40 mg *vs*. 0.25 μg of tellurium(IV) by sodium borohydride, or 0.25 μg tellurium(VI) by titanium(III) chloride–sodium borohydride reduction system. No separation or preconcentration technique is required for the determination of ppm level of tellurium in iron matrix, if there is no other interfering ion. The standard steel was dissolved by the following procedure; 0.1 g steel was weighed precisely in a 50 cm^3 beaker. After addition of 3 cm^3 of hydrochloric acid and 1 cm^3 of nitric acid, the mixture was heated on a water bath, and the steel was dissolved. The solution was diluted to 50 cm^3 with water in a measuring flask after cooling. A prescribed volume of this solution was transferred to the reaction vessel and determination was carried out by means of the titanium(III) chloride–borohydride reduction (Table 3). The procedure could be completed within 30 min. Almost the same results were obtained in the standard addition and calibration curve techniques.

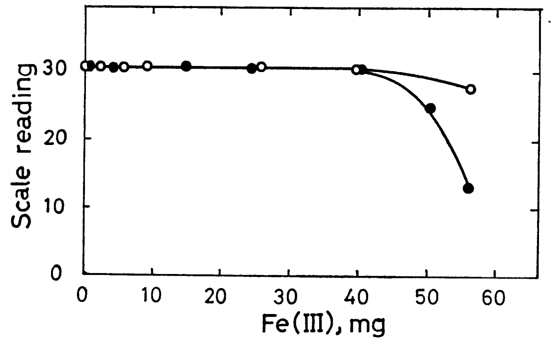

Fig. 5. Effect of iron(III) on the determination of tellurium.
-○- Te(IV) 0.25 μg/3 mol dm^{-3} HCl, 5% w/v $NaBH_4$, 5 cm^3. -●- Te(VI) 0.25 μg/3 mol dm^{-3} HCl, 5% w/v $TiCl_3$, 2 cm^3 (prereduction time, 40 s) 5% w/v $NaBH_4$, 5 cm^3.

Determination of Tellurium in Sulfur. The proposed technique was also applied to the determination of tellurium in commercial reagent sulfur. The results are given in Table 4. The modified procedure of Arikawa[12] was used: Sulfur powder (*ca*. 0.1 g) was weighed in a teflon beaker; 5 cm^3 of 3 mol dm^{-3} sodium hydroxide solution was added, and the mixture was heated on a hot plate (*ca*. 150 °C) in order to dissolve the powder. After cooling, 20 cm^3 of water was added, followed by 4 cm^3 of 30% w/v hydrogen peroxide solution to oxidize sulfur to hexavalent (tellurium is also oxidized to hexavalent). Excess hydrogen peroxide was then decomposed by careful heating. Finally, 10 cm^3 of hydrochloric acid was added, and the solution was diluted to 100 cm^3 with

Table 3. Determination of tellurium in steel

Sample	Taken(g)	Te		Certified
		Found (g)[a]	%	%
Tellurium-1[b]	0.0585	3.5	0.0059	0.0056_3
	0.1040	5.8	0.0056	
	0.1255	6.9	0.0055	
		average	0.0056_7	
Tellurium-2[b]	0.1052	8.0	0.0076	0.0075_3
	0.1140	8.2	0.0072	
	0.1088	8.1	0.0074	
		average	0.0074	
A[b]	0.1095	22	0.020	0.02[c]
	0.1070	21	0.020	
	0.4456	85	0.019	
	0.3588	75	0.021	
	1.0239	200[d]	0.020	
	1.0107	208[d]	0.021	
	2.0122	390[d]	0.019	
		average	0.020	
B[b]	0.3390	332	0.098	0.10[c]
	0.5233	512	0.098	
	0.3524	573	0.103	
		average	0.099_7	

a) Average of three determinations. b) Supplied by Japan Steel Works, Ltd. (Muroran Plant). c) Tellurium content of the sample. d) Separated from iron matrix by tin(II) chloride precipitation procedure.

Table 4. Determination of tellurium in reagent sulfur

Sample		Te		
Form	Taken(g)	Found(μg)	%	
Powder	0.1047	3.8_1	0.003_6	mean= 0.003_6
	0.0664	2.5_3	0.003_8	
	0.1103	4.3_0	0.004_0	
	0.0616	2.0_9	0.003_4	
	0.1015	3.4_5	0.003_4	
	0.1014	7.7	(4 μg of Te was added)	
	0.0983	10.1	(6 μg of Te was added)	
Sublimed	0.1017	1.9_0	0.001_9	0.002_0
	0.1044	2.1	0.002_0	
Colloidal	0.5041	0.08	0.00002	
	0.3172	0.07	0.00002	
Crystalline	0.6718		<0.00001	
	0.5108		<0.00001	

a) Average of three determinations

water. An adequate volume of the solution was transferred to the vessel and the tellurium was determined by titanium(III) chloride–borohydride reduction system (2 cm^3 of 5% w/v titanium(III) chloride for 1 min of prereduction time). Though the titanium(III) chloride–borohydride reduction system cannot be applied to sulfuric acid medium, the presence of 2 mmol sulfuric acid in 3 mol dm^{-3} hydrochloric acid caused no interference. The standard addition technique and calibration technique gave almost the same results.

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