Spectrophotometric Determination of Tellurium(IV) by Extraction with Tributylphosphate

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Several spectrophotometric methods for tellurium determination have been reported[1-7]. However these methods have still some disadvantages, e. g. troubles in separation by precipitation.

In the study of separation of tellurium from iron[8], the authors have found that tellurium(IV) complex with thiourea is extracted by tributylphosphate (TBP) from a dilute hydrochloric acid solution in the presence of potassium thiocyanate and the yellow color develops more deeply in the TBP phase than in the aqueous phase. When thiourea or potassium thiocyanate exists alone in the solution, tellurium complex is not extracted by TBP, whereas in case where a large excess of thiocyanate ions exists in the solution whose hydrochloric acid concentration is more than 0.1 N, even a small amount of tellurium is extracted by TBP. The coloration thus developed in TBP was applied to the spectrophotometric determination of tellurium.

Experimental

Reagents, Materials and Apparatus.—*Hydrochloric acid and nitric acid.*—A guaranteed reagent is diluted with pure water to the required concentrations.

Potassium thiocyanate solution.—The guaranteed reagent 500 g. is dissolved in pure water and diluted to 1000 ml.

Thiourea solution.—The guaranteed reagent 80 g. is dissolved in water at 70°C and diluted to 1000 ml.

Standard solutions of tellurium(IV).—Metallic tellurium (2 g.) supplied by Nippon Kogyo Co. Ltd., is dissolved in 30 ml. of aqua regia and the solution is evaporated on a water bath. Concentrated hydrochloric acid (10 ml.) is added to the residue and the liquid is evaporated to dryness; this procedure is repeated twice in order to expel any traces of nitric acid from the solution. The residue is again dissolved in hydrochloric acid and diluted with pure water. By this procedure two solutions of tellurium are prepared as a stock solution, i. e., 6 N hydrochloric acid solution containing tellurium in a concentration of 10 g./l. and 3 N hydrochloric acid solution containing 2 g. Te/l. Several standard series of tellurium are prepared by diluting one of these stock solutions with dilute hydrochloric acid.

n-Tributyl phosphate (TBP).—TBP is purified by the method reported by Alock et al.[9], and used without dilution after saturation with the reagent solutions under experimental conditions.

A Beckman DU spectrophotometer with 10 mm. cell was used for the measurements of absorbances. pH values were determined by Horiba H-type pH-meter with a glass electrode.

Procedure.—The same volume of TBP with that of the sample solution was used for a single extraction without any organic diluent. Although under the experimental conditions tellurium complex is extracted completely with TBP by shaking in a separatory funnel for 30 sec. The shaking was continued for 2 min. to ensure the extraction. The extraction was carried out only at room temperature.

After extraction, both TBP- and aqueous-phase became turbid to some extent, the extent depending on the initial acidity of the aqueous solution. A clean solution, however, was obtained by centrifuge; this treatment gave no remarkable volume change of the two phases.

Potassium thiocyanate solution is added to a sample solution whose pH was controlled to about 1, to which thiourea solution is added. The solution is finally fitted to a constant volume (10 or 20 ml.) and the pH value adjusted to 1 with hydrochloric acid. After 20 min., the same volume of TBP as that of the aqueous solution is added and the mixture shaken for 2 min. with a shaker. When the TBP phase is separated from the aqueous phase, the former is taken out with a centrifugal separator and the absorbance of tellurium(IV) complex in TBP is measured at 400 mμ.

Results and Discussion

Absorption Spectrum of Tellurium(IV) Complex in TBP.—Hydrochloric acid solutions containing 20, 50 and 100 γ of tellurium per ml. were prepared, and to its 10 ml. portion were added 5 ml. of potassium thiocyanate solution and 4 ml. of thiourea solution. The

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solution was made pH 1.0 with hydrochloric acid and made up to 20 ml. with 0.1 N hydrochloric acid. After 20 min., 20 ml. of TBP was added to the solution, and this mixture was shaken for 2 min. so that the tellurium complex could be extracted to the TBP phase thoroughly. The TBP phase was colored more deeply yellow than that obtained by the use of thiourea solution alone. This coloration was stable at least for 2.5 hr. The absorbance of the solution was measured spectrophotometrically over the range of wavelength, 330 mμ to 560 mμ. The results are shown in Fig. 1.

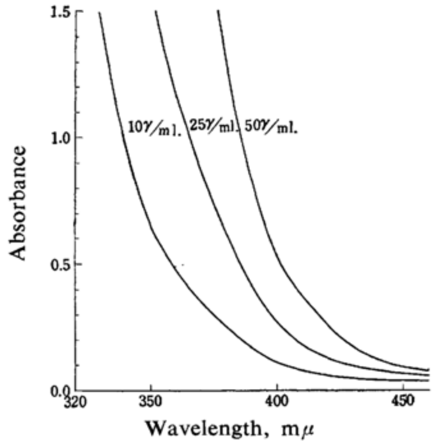

Fig. 1. Absorption curves of tellurium(IV) complex in TBP. KSCN 5 ml., $(NH_2)_2CS$ 4 ml., pH 1, total volume 20 ml., TBP 20 ml.

As shown in Fig. 1, tellurium complex in TBP has strong absorption in ultraviolet region. Although these absorption spectra are similar to those of tellurium-thiourea complex in dilute hydrochloric acid solution, absorbances of the former are several times greater than those of the latter.

Effect of Potassium Thiocyanate.—Varying amounts of potassium thiocyanate solution were added to solutions each containing 500 γ of tellurium and 4 ml. of thiourea solution. The pH of the solutions was kept about 1. The final volume of each solution was then made up to 20 ml.

Table I shows the absorbance of these solutions as a function of the amount of the reagent added. Constant absorbances were obtained adding more than 2 ml. of the reagent solution; one gram of the reagent, therefore, is sufficient for extracting thoroughly 500 γ of tellurium. To refer the effect of potassium thiocyanate on the extraction of tellurium, the amounts of tellurium remaining in the aqueous phase were determined also by thiourea method and the percentages of tellurium extracted were calculated from those values. The results agree with those obtained by the absorbance measurements.

In the absence of potassium thiocyanate, tellurium complex is not extracted with TBP under the experimental condition. However when potassium thiocyanate exists together with thiourea in the tellurium solution, percentage of the extracted tellurium increases with increasing amount of the reagent added, and the tellurium complex is extracted almost completely with TBP, when more than 1 ml. of the reagent is added.

TABLE I. EFFECT OF POTASSIUM THIOCYANATE

KSCN solution ml.	Absorbance of TBP-phase at 400 mμ	Te Taken	 Found, aq. phase	 Extracted
		γ	γ	%
—	0.000	500	497	0.6
0.01*	0.004	500	479	4.8
0.02*	0.013	500	450	10.0
0.05*	0.037	500	398	20.4
0.5	0.221	500	47	90.6
1.0	0.262	500	7.5	98.5
2.0	0.278	500	0.5	99.9
4.0	0.279	500	0.5	99.9
8.0	0.284	500	0.0	100

Thiourea solution 4 ml., pH 1, total volume 20 ml., TBP 20 ml.

* Added after dilution of the stock solution.

Effect of Thiourea.—Since the amount of thiourea also affects the color development of tellurium complex in dilute hydrochloric acid solution, several experiments were carried out to determine its effect. Measurements of the absorbance of the TBP phase showed that 80 mg. of thiourea is sufficient for complexing thoroughly 500 γ of tellurium and absorbances are constant beyond this concentration of thiourea.

In order to ensure the results, the amounts of tellurium remaining in the aqueous phase were determined and the percentage of tellurium extracted into TBP phase was calculated. (Table II) The results agree with those obtained by the absorbance measurements.

TABLE II. EFFECT OF THIOUREA

Thiourea solution ml.	Absorbance of TBP-phase at 400 mμ	Te Taken	 Found, aq. phase	 Extracted
		γ	γ	%
—	0.002	500	420	16
0.5	0.071	500	289	42
1	0.277	500	2	99.6
2	0.278	500	0	100
3	0.276	500	4	99.2
5	0.277	500	0	100
8	0.276	500	2	99.6

Potassium thiocyanate solution 2 ml., pH 1, total volume 20 ml., TBP 20 ml.

Effect of pH.—In view of possible decomposion of either potassium thiocyanate or thiourea in an acid solution, experiments were carried out in low acidity solutions. A series of solutions were prepared, containing 500 γ of tellurium, 2 ml. of potassium thiocyanate solution and 2 ml. of thiourea sulution. The pH values of these solutions were controlled around 1 with hydrochloric acid and similarly extracted with TBP. Results are shown in Table III. The absorbance at 400 mμ remains constant in the range from pH 0.6 to 1.7, indicating that tellurium complex is extracted with TBP so that it is possibe to extract and determine tellurium over this pH range.

TABLE III. EFFECT OF pH

pH values before extraction	Absorbance of TBP-phase at 400 mμ	Te	
		Found, aq. phase γ	Extracted %
0.34	0.262	2	99.6
0.6	0.275	0	100
1.0	0.278	0	100
1.3	0.277	1	99.8
1.7	0.275	2	99.6

Te 500 γ, KSCN soln. 2 ml., thiourea soln. 2 ml., total volume. 2 ml., TBP 20 ml.

Stability of Color.—The yellow color of tellurium complex extracted into TBP phase is very stable and is several times as deep as that of the complex formed with thiourea in dilute hydrochloric acid solution. Four solutions containing 5, 12.5, 25 and 50 γ of tellurium per milliliter respectively were prepared and, after extraction, the stability of the color of each solution was tested. No changes were found in the absorbance after exposure in diffused light for 150 min.

Recommended Procedure.—To 15 ml. of a sample solution (ca. 0.1 N hydrochloric acid solution containing up to 500 γ of tellurium), add 2 ml. of potassium thiocyanate solutions (500 g./l.) and 2 ml. of thiourea solution (80 g./l.). Adjust pH to 1, and make the final volume of the solution to 20 ml. with 0.1 N hydrochloric acid. After 20 min. add 20 ml. of TBP to the solution, and shake for 2 min.

When the TBP phase separates from the aqueous phase, centrifuge the former for 2 min. The absorbance of TBP phase is measured at 400 mμ with a spectrophotometer with 10 mm. cells.

Calibration Curves.—Prior to the determination of tellurium in the sample solution, calibration curves were prepared with a series of solutions containing 1 to 75 γ of tellurium per milliliter. The curves are shown in Fig. 2.

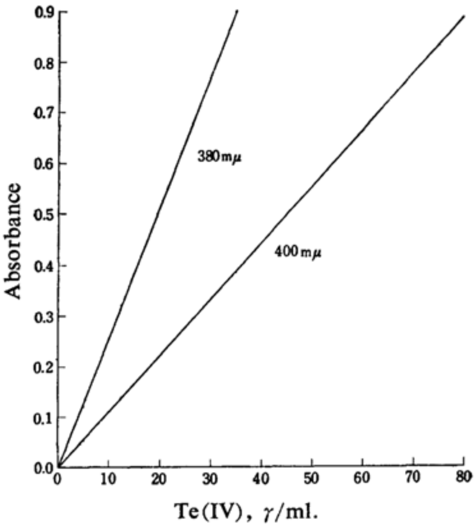

Fig. 2. Calibration curve for tellurium.

TABLE IV. ANALYSIS OF SAMPLES OF TELLURIUM

Absorbance vs. blanc	Te		Difference γ
	added γ	found γ	
0.277	250	249	−1
0.275	〃	247	−3
0.277	〃	249	−1
0.279	〃	251	1
0.278	〃	250	0
0.270	〃	243	−7
0.282	〃	254	4
0.285	〃	257	7
0.273	〃	247	−3
0.279	〃	251	1
	mean	249.7	−0.2
0.552	500	497	−3
0.553	〃	498	−2
0.570	〃	514	14
0.556	〃	501	1
0.539	〃	485	−15
0.544	〃	490	−10
0.546	〃	492	−8
0.552	〃	497	−3
0.564	〃	508	8
0.558	〃	503	3
0.545	〃	491	−9
0.548	〃	494	−6
0.554	〃	499	−1
0.546	〃	492	−8
0.565	〃	509	9
0.554	〃	499	−1
0.548	〃	494	−6
0.558	〃	503	3
0.564	〃	508	8
0.546	〃	492	−8
	mean	498.3	−1.7

TABLE V. INTERFERENCE STUDY OF DIVERSE IONS ON ABSORBANCE OBTAINED WITH 25 p.p.m. OF TELLURIUM

Ions present	Added as	Concentration p.p.m.	Difference of absorbance ×1000	Tolerance p.p.m.
Bi^{3+}	$Bi(NO_3)_3$	2.5	21	0
		5.0	36	
Cu^{2+}	$CuSO_4$	10	0	10
		25	7	
		100	34	
Ni^{2+}	$Ni(NO_3)_2$	50	0	50
		125	4	
		250	16	
Te^{6+}	Na_2TeO_4	75	6	75
Co^{2+}	$CoCl_2$	50	−2	500
		500	−3	
Fe^{3+}	$FeCl_3$	0.3	0	0.3
		0.9	20	
Cr^{3+}	$CrCl_3$	50	2	50
		250	7	
Hg^{2+}	$HgCl_2$	400	1	large excess
Zn^{2+}	$ZnCl_2$	50	0	500
		500	−3	
Cd^{2+}	$CdCl_2$	500	0	large excess
Mn^{2+}	$MnSO_4$	250	0	〃
Al^{3+}	$AlCl_3$	500	0	〃
Mg^{2+}	$MgCl_2$	50	0	〃
		500	−2	
PO_4^{3-}	H_3PO_4	1400	0	〃
SO_4^{2-}	H_2SO_4	1250	−2	〃
NO_3^-	HNO_3	500	0	〃
WO_4^{2-}	Na_2WO_4	50	−1	50
		500	−45	
VO_3^-	NH_4VO_3	10	3	10
		50	17	
CrO_4^{2-}	K_2CrO_4	50	−54	0

A linear relationship exists between the absorbance and the tellurium concentration over the range investigated. In many respect, however, measurement at 400 mμ is preferable to that at 380 mμ.

Reproducibility.—Several samples were prepared separately in the same way as unknown samples and analysed by the recommended procedure. As shown in Table IV, the reproducibility of this procedure is satisfactory.

Effect of Diverse Ions.—Separate tests were made to elucidate the interference of various cations as well as anions on the tellurium determination. The results are shown in Table V. In this table, by " tolerance " is meant the value that gives no significant interference. Under these values the difference between the absorbance of tellurium of the test solution and that of the standard containing no other ions is less than 3%.

A pre-extraction test was also made in which a previous attempt to remove Bi^{3+}, Cu^{2+}, Ni^{2+} and Fe^{3+} was made, since these ions were considered to have relatively larger interfering behavior. In this experiment, only potassium thiocyanate and no thiourea was added first to the solution of tellurium containing these ions. After a single extraction with the same volume of TBP at pH 1, the organic layer was separated off and the remaining aqueous solution was used to determine the amount of tellurium. Some more potassium thiocyanate and also a necessary amount of thiourea were added to this aqueous solution ; tellurium was shaken out to the TBP layer according to the recommended procedure, and then determined spectrophotometrically. As shown in Table VI, a single pre-extraction treatment is not sufficient to give a satisfactory value for tellurium, since about 6% positive error results in the absorbance of tellurium. This means that even after the pre-extraction, there remain some fractions of these ions which are transferred to the TBP layer when the recommended procedure is applied. In the single pre-extraction, Cu^{2+} and Ni^{2+} seems to be extracted only partly although Fe^{3+} and Bi^{3+} may be extracted fairly well. It would be possible, however, to eliminate them to such an extent that they give little effect on the determination of tellurium, if a better experimental condition were further sought.

TABLE VI. PRE-EXTRACTION TEST

Te taken p.p.m.	Ions added p.p.m.	Absorbance at 400 mμ in TBP
25	—	0.139
25	Bi^{3+} 5 Cu^{2+} 25 Ni^{2+} 50 Fe^{3+} 1.3	0.147
—	Bi^{3+} 5 Cu^{2+} 25 Ni^{2+} 50 Fe^{3+} 1.3	0.006

Summary

Spectrophotometric determination of tellurium(IV) by means of extraction with 100% TBP was studied. Tellurium forms yellow complex, as seen in the literature, with thiourea in a dilute hydrochloric acid solution, and the complex is extracted into TBP whenever potassium thiocyanate is present in excess in the solution.

Conditions on the extraction and the determination of tellurium were examined. It was found that addition of 2 ml. of thiourea solution (80 g./l.) and 2 ml. of potassium thiocyanate solution (500 g./l.) to the sample solution is enough to extract 1 to 500 γ of tellurium per 20 ml. from the dilute hydrochloric acid solution with 20 ml. TBP. Tellurium complex was extracted thoroughly with TBP at pH 1. For the determination of tellurium, the absorbance of the TBP phase was measured spectrophotometrically at 400 mμ.

The effect of the diverse ions on the absorbance of tellurium complex was examined and also pre-extraction test on the removal of interference ions was carried out.

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