The Separation of Trace Amounts of Tellurium from Iron by Solvent Extraction

By Yasumitsu UZUMASA, Kenjiro HAYASHI and Saburo ITO

(Received October 26, 1962)

According to the standard method of the Japan Institute of the Promotion of Science and Techniques[1], when a steel sample containing tellurium is treated with a mixture of ammonium hydrogen fluoride and sulfuric acid, most of iron goes into solution while tellurium, silica, carbon, etc., together with a little iron, are left undissolved. This method of dissolving can be applied to a sample containing as much as 0.1 mg. of tellurium. When we investigated this method in detail, our experiments revealed, however, that when the tellurium content is less than this amount, the separation of tellurium from iron is never complete. It was found that a part of the tellurium passes through the filter paper, the amount of tellurium in the residue being thus reduced. After these studies, therefore, we abandoned this procedure and investigated another method in which tellurium, together with iron, is dissolved in a suitable solvent and the former is separated from the latter by the extraction method.

Experimental and Results

Apparatus.—A Beckman model DU spectrophotometer with 1 cm. silica cells was used.

Procedure.—One gram of solid thiourea is added to 15 ml. of the sample solution; this is equivalent to 2 N of a hydrochloric acid concentration. After the mixed solution is made up to 20 ml. with 2 N hydrochloric acid, it is allowed to stand for 20 min. and absorbance is measured at 350 or 370 mμ[2,3].

---

[1] The Japan Institute of the Promotion of Science and Techniques, "Rapid Analysis of Iron and Steel", Maruzen, Tokyo (1956), p. 247.

[2] Kazuo Ota, *J. Japan Inst. Metals*, **23**, 581 (1959).

[3] D. F. Boltz, "Colorimetric Determination of Nonmetals", Interscience Pub. Inc., N. Y. (1958), p. 309.

Change in the State of Tellurium During the Dissolution of the Steel Sample. — As to the state of a minute amount of tellurium in steel, very little consideration has been paid it so far. As may be seen from the Fe–Te diagram (Fig. 1)4), it is quite possible that it exists as $FeTe_{0.90}$. Iron telluride of this niccolite type may produce, by the action of an acid, hydrogen telluride, which may further yield metallic tellurium as indicated by the following equation:

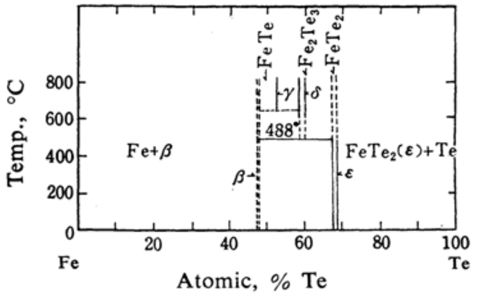


Fig. 1. Fe–Te diagram.
The phase: $FeTe_{0.90}$
The phase: $FeTe_{1.1}$
The phase: $FeTe_{1.4}-FeTe_{1.5}$
The phase: $FeTe_2$

$$H_2Te(aq) = Te + 2H^+ + 2e$$

$$E^\circ_{298} = +0.69\ \mathrm{V}.$$ 5)

It is also possible that a part of the hydrogen telluride thus produced might remain not oxidized and volatilize as gas, since its boiling point is $-1.8\sim0$°C at 1 atm.6) In order to examine this possibility, 5 g. of the steel sample containing 0.3 mg. Te/g. was dissolved in 6 N hydrochloric or sulfuric acid and the gas evolved was introduced into ammonia. The amount of tellurium absorbed in ammonia was found always to be less than 10 μg. This indicates that the volatilization may be disregarded.

Another possibility is that in acidic media metallic tellurium might be oxidized by ferric iron to tellurium(IV) and dissolve into the solution:

$$Te + 2H_2O \rightleftharpoons TeO_2 + 4H^+ + 4e \qquad E^\circ_{298} = -0.529\ \mathrm{V}.$$ 5)

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e \qquad E^\circ_{298} = -0.771\ \mathrm{V}.$$

Therefore, metallic tellurium suspended in a acidic medium will more or less dissolve in the presence of iron(II) as the latter is oxidized to iron(III) by air. This was confirmed by the following experiment.

The precipitate of metallic tellurium prepared by adding stannous chloride to a hydrochloric acid solution of potassium tellurite was centrifuged and washed with water thoroughly. When this precipitate was suspended in 6 N hydrochloric acid containing ferric chloride, rapid dissolution of the precipitate took place. It is, therefore, possible that, in the practical analysis of steel, the existence of ferric iron brings about the solution of metallic tellurium, if it is present. The time necessary for the complete dissolution of steel samples differs according to type. In cases where it takes a longer time, the partial oxidation of iron(II) to iron(III) occurs, resulting in a partial dissolution of the metallic tellurium. This is illustrated in Table I.

TABLE I. DISSOLUTION OF METALLIC TELLURIUM WITH FERRIC IRON IN HYDROCHLORIC OR SULFURIC ACID

Sample No.	Acid	Dissolving time, min.	Tellurium In the sample, mg.	Tellurium In the soln., μg.
1	HCl	8	1.03	4.3
2	HCl	18	0.695	7.7
3	HCl	20	0.45	16.5
4	HCl	90	1.35	610.0
1	H_2SO_4	10	1.03	25.3
2	H_2SO_4	17	0.695	12.1
3	H_2SO_4	20	0.45	4.3
4	H_2SO_4	30	1.35	0

Acid concentration: 6 N
Volume of the solution: 25 ml.
Steel sample taken: 1 g.

When sulfuric acid was used, the steel sample dissolved more rapidly and the particles of metallic tellurium coagulated in larger aggregates. Moreover, the oxidation of ferrous iron in sulfuric acid is more difficult.

Reexamination of the Precipitation Method. —There is a conventional method of separation in which the steel sample containing tellurium is dissolved in a suitable solvent and the solution is treated with such a reducing agent as stannous chloride and then the tellurium is reduced and precipitated. The precipitate is filtered off, the tellurium being thus separated from the iron. A critical examination of this method was undertaken.

Ten grams of solid stannous chloride were added to 150 ml. of 3 N hydrochloric acid containing sodium tellurite equivalent to 66 μg. of tellurium. The solution was then boiled

---

4) M. Hansen and K. Anderko, "Constitution of Binary Alloys", McGraw-Hill Book Co. Inc., N. Y. (1958), p. 722.

5) W. M. Latimer, "The Oxidation State of the Elements and Their Potentials in Aqueous Solutions", 2nd. Ed., Prentice-Hall, N. Y. (1956).

6) "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", XI, Longmans, London (1931), p. 63.

for 5 min. After the liquid had been allowed to stand for one hour at room temperature, the precipitate formed was filtered through Toyo No. 5C filter paper and washed with hydrochloric acid. The precipitate was then brought into solution by nitric acid, and the amount of tellurium was determined spectrophotometrically with thiourea. The results are shown in Table II.

TABLE II. FRACTION OF PRECIPITATED TELLURIUM

Tellurium, μg.		Recovery %
Taken	Found	
66.0	30	45.5
66.0	26	39.4
66.0	25	37.9
66.0	25	37.9
66.0	24	36.4
66.0	24	36.4
	Ave.	39.0

It is obvious from this table that this precipitation method can not be applied to a sample whose tellurium content is very small.

Extraction of Tellurium with an Organic Solvent. — Ferric iron in highly concentrated hydrochloric acid can be extracted quite efficiently with some organic solvents such as ethyl acetate, *n*-butyl acetate or methyl isobutyl ketone, while the extractability of tellurium under similar conditions has not previously been well known. Tellurium(IV) is oxidized into tellurium(VI) by potassium dichromate. It has already been confirmed by the authors that, in a highly concentrated hydrochloric acid solution, the behavior of the tellurium thus oxidized is remarkably different from that of ordinary tellurate ions[7]. Accordingly, it is expected that the extractability of tellurium(VI) formed with potassium dichromate into ethyl acetate, *n*-butyl acetate or methyl isobutyl ketone will differ from that of tellurite or tellurate. Therefore, experiments on the extractability of tellurium into the above-mentioned solvents were carried out under various conditions.

Twenty milliliters of a 6 N or 9 N hydrochloric acid solution containing a definite amount of tellurium, together with or without potassium dichromate, was placed in a separatory funnel whose capacity was 100 ml. To this was added 10 ml. of an organic solvent. After 10 sec. shaking, the two layers were separated. The aqueous layer was evaporated to dryness on the water-bath. The tellurium in the organic solvent was extracted back into water, and the aqueous solution thus obtained was also evaporated to dryness. After dissolving each of these two residues, the amount of tellurium in each of them was measured by the spectrophotometric method using thiourea and the extractability of the element was calculated. When potassium dichromate was present, 1 ml. of 30% hydrogen peroxide was added to the aqueous solution, and, after being evaporated to dryness, each residue was dissolved in 6 N hydrochloric acid. When this acid solution was shaken with methyl isobutyl ketone, tellurium went into the organic solvent quantitatively. After the organic layer had been washed twice with 6 N hydrochloric acid, the tellurium in the organic layer was extracted back again into water and determined spectrophotometrically. The extractability is summarized in Table III.

As shown in Table III, of the three solvents used, *n*-butyl acetate seemed to be most suitable since the extractability of tellurium into this

TABLE III. EXTRACTABILITY OF TELLURIUM WITH VARIOUS ORGANIC SOLVENTS

Tellurium taken as	μg.	Concn. of HCl, N	5% $K_2Cr_2O_7$ ml.	Extractability, %		
				Ethyl acetate	*n*-Butyl acetate	Methyl isobutyl ketone
Na_2TeO_3	330	6	0	63	19.4	100
Na_2TeO_3	330	6	0	62	18.4	100
Na_2TeO_3	330	6	1	54	11.0	100
Na_2TeO_3	330	6	1	51	12.7	100
Na_2TeO_3	330	9	0		34.6	
Na_2TeO_3	330	9	0		36.2	
Na_2TeO_3	330	9	1		22.5	
Na_2TeO_3	330	9	1		25.0	
Na_2TeO_4	200	6	0		1.6	2.6
Na_2TeO_4	200	6	0		1.7	2.7
Na_2TeO_4	200	9	0		3.0	
Na_2TeO_4	200	9	0		3.1	

---

[7] Y. Uzumasa, S. Hikime, K. Hayashi and H. Yoshida, *Japan Analyst* (*Bunseki Kagaku*), **11**, 78 (1962).

solvent is the smallest. It was also observed that potassium dichromate tends to reduce the extractability of the element. Accordingly, further experiments were carried out to study the extractability in detail, varying the concentration of hydrochloric acid over a wide range. The results are shown in Table IV.

TABLE IV. EFFECTS OF DICHROMATE AND HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTABILITY OF TELLURIUM WITH *n*-BUTYL ACETATE

Concn. of HCl, N	Extractability of tellurium, %	
	1 ml. of 5% $K_2Cr_2O_7$ added	Without $K_2Cr_2O_7$
3	0.7	2.5
3	1.5	2.7
3	1.8	2.8
6	12.7	18.8
6	12.7	19.0
6		19.4
7.5	19.4	22.4
7.5	20.4	25.0
7.5	20.4	25.6
9	22.5	34.6
9	25.0	36.5
9	26.3	
10.5	41.0	55.8
10.5	44.7	55.2

Tellurium taken: 330 μg.

It has been known that the ferric iron is extracted from a concentrated hydrochloric acid solution into *n*-butyl acetate quite rapidly and quantitatively. When, for example, 20 ml. of 9 N hydrochloric acid containing 1 g. of ferric iron was treated with 10 ml. of *n*-butyl acetate, 99.8% of the iron(III) was found to be removed. Only 1.7 to 2.0 mg. of ferric iron remained in the hydrochloric acid layer after one extraction. Accordingly, this process possibly allows for the separation of a minute amount of tellurium from a large amount of iron.

The extraction of a small quantity of tellurium(IV) with methyl isobutyl ketone was also studied. Table V shows the results, which agree fairely well with those obtained by Goto et al.[8], who investigated the extractability of many metals by this solvent.

When the concentration of hydrochloric acid was adjusted to a normality of 4.5 to 6, tellurium(IV) was extracted into this liquid quantitatively, whereas chromium(III) was not removed at all under the same conditions. This fact suggests that tellurium(IV) and chromium(III) may be separated from each other by this extraction.

TABLE V. EFFECT OF THE HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTABILITY OF TELLURIUM WITH METHYL ISOBUTYL KETONE

Concn. of HCl, N	Extractability of tellurium, %
3	86.5
3	81.7
4.5	99.3
4.5	99.3
4.5	100.0
6	99.3
6	99.3
6	100.0
6	100.0
7.5	98.2
7.5	98.2

Tellurium taken: 330 μg.

The Separation of Iron and Tellurium with *n*-Butyl Acetate and Methyl Isobutyl Ketone.— It is clear from Table III that tellurium is partly extracted into *n*-butyl acetate when conditions allow a complete extraction of ferric iron. Therefore, further experiments were carried out to find a means of drawing a little tellurium extracted to the aqueous layer back again, leaving ferric iron in the organic layer.

Twenty milliliters of a 9.5 N hydrochloric acid solution containing 330 μg. of tellurium and 1 ml. of 5% potassium dichromate solution was shaken with 10 ml. of *n*-butyl acetate; nearly 30% of the tellurium was extracted into this organic layer. After being separated, the *n*-butyl acetate layer was washed several times with a 5 ml. portion of 9 N hydrochloric acid containing 1 ml. of 5% potassium dichromate. The results are shown in Table VI.

As is evident from Table VI, the tellurium in the organic layer can be shaken completely back to the aqueous layer in three back washings. Another trouble occurred, however, when, by this procedure, ferric iron also turned back, though only slightly, to the aqueous layer. Experiments were repeated, therefore, to find out a means of overcoming this difficulty. Finally the following scheme, by which a fairly satisfactory result was obtained, was obtained.

TABLE VI. BACK WASHING OF TELLURIUM(IV) FROM THE ORGANIC LAYER

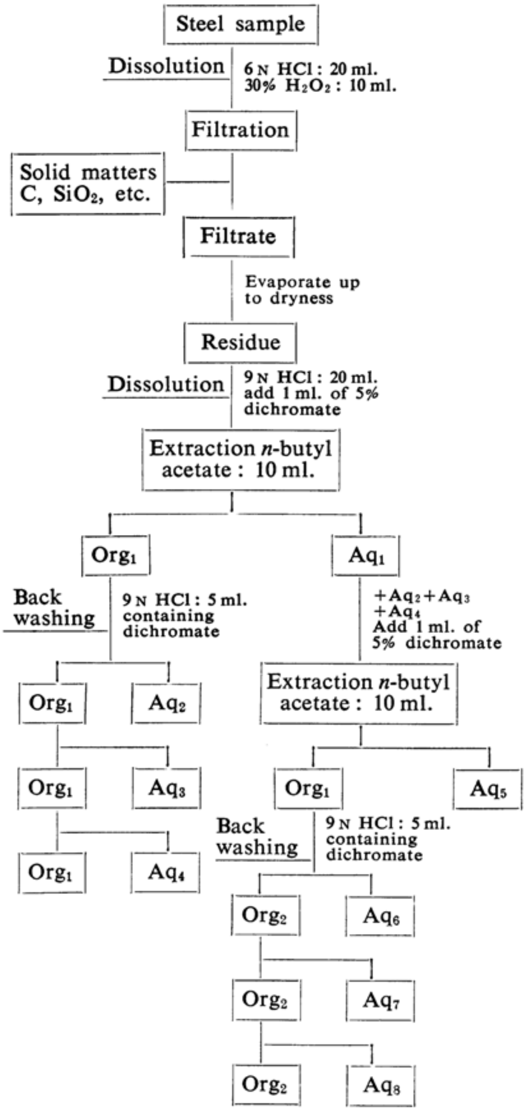
No. of back washing	Tellurium remaining in the organic layer, %	
0	33.2	30.0
1	13.0	11.0
2	5.6	4.5
3	1.5	0.0

Back washing solution: 5 ml. of 9 N hydrochloric acid containing 1 ml. of 5% potassium dichromate.

---

[8] H. Goto, Y. Kakita and H. Furukawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 1513 (1959).

TABLE VII. SCHEME OF THE SEPARATION PROCEDURE FOR TELLURIUM FOR STEEL



According to this scheme, tellurium is concentrated in the combined aqueous solution ($Aq_5+Aq_6+Aq_7+Aq_8$); the amount of iron in this solution is negligible. Chromium(III) as well as chromium(VI) are enriched in this aqueous layer, so that the removal of this element is necessary prior to the determination of the tellurium. Extraction with methyl isobutyl ketone is recommended for this purpose. The procedure is as follows:

Two milliliters of 30% hydrogen peroxide is added to a hydrochloric acid solution containing tellurium, together with chromium as a dichromate. After chromium(VI) is reduced to chromium(III), the excess of hydrogen peroxide is decomposed by heating and the total volume of the solution is regulated to 20 ml. The acid concentration is adjusted to a normality of 4.5 to 6, and the tellurium is extracted with 10 ml. of methyl isobutyl ketone. One extraction is sufficient for the complete separation of the two elements. The tellurium extracted into the organic layer is successfully transferred back to the aqueous layer by treating it twice with 5 ml. of distilled water. Iron does not interfere in the spectrophotometry since the amount of this metal behaving with tellurium is less than 0.1 mg., even when 1 g. is contained in the original solution. Table VIII shows that a large amount of ferric iron can be separated from tellurium(IV) by this method.

TABLE VIII. SEPARATION OF TELLURIUM FROM IRON

Fe^{3+} Added mg.	Tellurium, μg. Taken	Tellurium, μg. Found	Recovery %
102	33	33.0	100
102	33	33.0	100
102	33	32.5	98.4
510	33	35.5	107.6
510	33	33.0	100
510	33	33.0	100
510	66	63.3	96.0
510	66	65.0	98.4
510	66	65.0	98.4
510	330	329	99.5
510	330	329	99.5
510	330	329	99.5
1020	33	37.5	115
1020	33	34.0	103
1020	66	67.5	102
1020	66	66.0	100
1020	66	65.2	98.8
1020	66	65.0	98.4
1020	330	319.0	96.7
1020	330	310.0	94.0
1020	330	319.0	96.7

Aqueous layer : 20 ml.; organic layer : 10 ml.; when 1.02 g. of iron was taken, aqueous layer : 40 ml. ; organic layer : 20 ml.

It has been made clear that our new method furnishes a quantitative means for separating iron and tellurium.

The Determination of Tellurium in Steel. — Since we had no standard sample at hand whose tellurium content was known, the same sample was analyzed both by our method and by the conventional precipitation method and the two results were compared for reference.

In our method, 0.5 g. of the steel sample was heated in a mixture of 20 ml. of 6 N hydrochloric acid and 10 ml. of 30% hydrogen peroxide until it dissolved; the insoluble matters

TABLE IX. COMPARISON BETWEEN THE TWO METHODS

Sample No.	Composition					Tellurium found, %*	
	C	Si	Mn	P	S	By extraction method	By p. p. t. method
1	0	0	0	0	0	0.102***	0.103
2	0	0	0	0	0	0.0695***	0.071
3	0	0	0	0	0	0.045***	0.045
4	0	0	0	0	0	0.135***	0.14
46	3.46	1.43	0.36	0.336	0.08	0.0113	0.0113
113	3.62	1.47	0.34	0.368	0.084	0.0128	0.013
122	3.44	1.38	0.36			0.012	0.0135
144	3.49	1.39	0.40	0.336	0.08	0.007	0.0072**
159	3.52	1.22	0.31	0.544	0.082	0.0077	0.008**

* Mean value of five determinations
** 2 g. of the sample taken
*** 0.1 g. of the sample taken

(carbon, silica, etc.) were then filtered off. After washing the residue with 10 ml. of 6 N hydrochloric acid, the filtrate, together with the washing, was evaporated to dryness on a water bath. The residue obtained was then treated according to the procedure described above.

As was pointed out above, in the precipitation method the amount of tellurium can not be determined accurately unless it is more than 0.1 mg. Therefore, we took many samples of at least 1 g. or more. The samples were dissolved in 20 to 30 ml. of 6 N sulfuric acid. When the solid matter nearly disappeared, 10 g. of stannous chloride was introduced. After having been left standing for 30 min., the solution was filtered and the solid remaining on the filter paper was washed with hydrochloric acid (1 : 10) containing stannous chloride and then with water. The washed precipitate of tellurium was dissolved in hot hydrochloric acid (1 : 2) containing hydrogen peroxide, the excess of which was decomposed by heating. After adjusting the acid concentration and the volume of the solution to about 3 N and 100 ml. respectively, tellurium was precipitated by adding 5 g. of stannous chloride. The results are summarized in Table IX. The two values are in good accord.

Conclusion

1) In the precipitation method, foreign substances existing in the solution tend to coprecipitate and lower results for tellurium are occasionally obtained, especially when the total amount of tellurium is less than 0.1 mg. The authors' method gives better results even when the amount of tellurium falls under this amount.

2) After being separated from iron, tellurium is determined by the spectrophotometric method with thiourea, i. e., by measuring the absorption at 350 and 370 mμ. In this procedure, the variety as well as the quantity of coexisting anions markedly affects the result of analysis, so they must be accurately regulated. When our extraction procedure is applied, however, these troubles are considerably minimized.

3) The amount of the sample to be taken in our method should preferably be not more than 0.5 g. If a larger amount is taken, some time-consuming treatment must be added and the rapidity of the method is lost.

Faculty of Science
Hokkaido University
Sapporo