Solvent Extraction Studies of Tellurium(IV) with Dithizone

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Dithizone (diphenylthiocarbazone, designated in this paper as H_2Dz) has previously been widely used for the extraction or the colorimetric determination of various metals. In a previous paper, one of the present authors reported that tellurium(IV), when shaken with a dithizone solution, was extracted into an organic layer, thus forming a complex compound with dithizone.1) Generally, however, relatively little is known about the species and about the nature of the tellurium complex which is extracted by organic solvents. Therefore, we investigated the behavior of tellurium(IV) in the solvent extraction process by using dithizone.

Experimental

Dithizone Solution. — The Merck product dithizone was purified by the ammonia water extraction method given by Sandell.2) The purity of dithizone in carbon tetrachloride was checked spectrophotometrically by the use of the ratio of E_{620}/E_{450}, where E_{620} and E_{450} stand for the extinction of dithizone at 620 and 450 mμ respectively.3) When this ratio is higher than 1.67, the solution may be considered sufficiently pure. The concentration of dithizone was determined spectrophotometrically each time it was used.

Carbon Tetrachloride.—Reagent-grade chemicals

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1) H. Mabuchi, This Bulletin, 29, 842 (1956).

2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, London (1959), p. 170.

3) S. S. Cooper and M. L. Sullivan, *Anal. Chem.*, 23, 613 (1951).

were distilled once, and the middle fraction of the distillate was used.

Ammonium Hydroxide.—A Concentrated C. P. reagent was distilled and absorbed in redistilled water. The ammonia solution used for the purification of dithizone was prepared by diluting this purified solution.

Hydrochloric Acid.—A concentrated C. P. reagent was distilled, and the middle fraction of the distillate was used.

Water.—Water was distilled twice in an all-glass distilling apparatus.

All other chemicals were of the reagent grade and were used without further purification.

The Preparation of a Tellurium Carrier Solution.—Tellurium dioxide was prepared from a tellurium crystal by the method described in "Inorganic Syntheses"[4]; then it was dissolved in acid solutions. The concentrations were determined gravimetrically.

The Preparation of Radioactive Tellurium.—Radioactive tellurium was produced by Sb (p, *x*n) reactions (x=1—4) by bombarding an antimony metal target with the 56 MeV. proton at the Institute for Nuclear Study, the University of Tokyo. After several weeks of cooling, carrier-free tellurium(IV) was separated from the antimony target by the dithizone-extraction method.[5] Since short-lived tellurium nuclides must already have decayed, the radioactive tellurium solution may be supposed to have been mainly composed of a mixture of Te-121m ($T_{1/2}$=154 d.) and Te-123 m ($T_{1/2}$=104 d.).

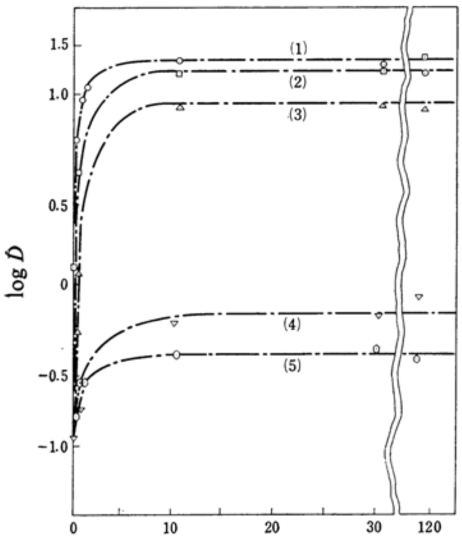

Fig. 1. Effect of shaking time on the extraction.

H_2Dz in CCl_4: —⊙— (1) 9.60×10^{-4} M, —⊡— (2) 2.00×10^{-3} M, —△— (3) 1.00×10^{-3} M, —▽— (4) 2.82×10^{-4} M, —⬡— (5) 1.20×10^{-4} M

$HClO_4$: (1) and (5) 2.43 M, (2), (3) and (4) 0.179 M

Shaking temp.: 20°C

Te(IV): ∼10^{-11} M

The Measurement of the Distribution Ratio.—Two milliliters of a carbon tetrachloride solution of dithizone was equilibrated by shaking it with 2 ml. of an aqueous solution containing tracer amounts of tellurium(IV) (∼10^{-11} M) for 30 min. in a 15-ml. flask with a glass-stopper at 25°C. One milliliter of each layer was then put into a test tube and its radioactivity measured with a well-type NaI scintillation counter. The distribution ratio, *D*, for tellurium(IV) is given by the radioactivity of the organic layer divided by that of the aqueous layer.

Similarly, with macro amounts of tellurium the distribution ratio was measured radiometrically by using radioactive tellurium as a tracer.

Spectrophotometric Measurements.—All absorptiometric works were carried out with a Cary recording spectrophotometer, model 14.

The Attainment of Equilibrium.—This was investigated by shaking a number of tubes, each containing 2 ml. of an organic layer and 2 ml. of an aqueous layer, for various lengths of time (Fig. 1). The equilibrium between the two layers was attained within about 10 min.

Results and Discussion

The Chemical Composition of the Tellurium Dithizonate in the Organic Layer.—The dependence of the distribution ratio, *D*, on the dithizone concentration in carbon tetrachloride, $(H_2Dz)_{org}$, was studied in the perchloric acid-sodium perchlorate media, using tracer amounts of radioactive tellurium. The results are shown in Fig. 2. It may be seen from Fig. 2 that the plot of $\log D$ vs. $\log (H_2Dz)_{org}$ at the constant $(H^+)_{aq}$ has a straight line whose slope is 2. This suggests, as is established below, that each tellurium(IV) cation in the organic layer is combined with two dithizonate anions.

In general, if one expresses the chemical species of tellurium in the acidic aqueous layer after the attainment of equilibrium as $(Te(OH)_n(HDz)_m)^{(4-m-n)+}$, and those in the organic layer as $Te(OH)_{4-p}(HDz)_p$, the slope of $\log D$ vs. $\log (H_2Dz)_{org}$, $\partial \log D/\partial \log (H_2Dz)_{org}=\bar{p}-\bar{m}$, where $\bar{m}$ and $\bar{p}$ are the average number of HDz^- per tellurium(IV) cation in the aqueous and organic layers respectively. Here polymerized species of tellurium are neglected. This assumption may be valid as far as tracer experiments of tellurium are concerned.

As HDz^- is a bidentate ligand, the coordination number, $N=4-p+2p$. From these considerations, one finds the two equations, (1) and (2):

$$\bar{p}-\bar{m}=2 \qquad (1)$$

$$p+4=N \qquad (2)$$

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[4] "Inorganic Syntheses," Vol. III, 143 (1950).

[5] Y. Yokoyama, H. Mabuchi, H. Shoji and N. Saito, This Bulletin, 36, 352 (1963).

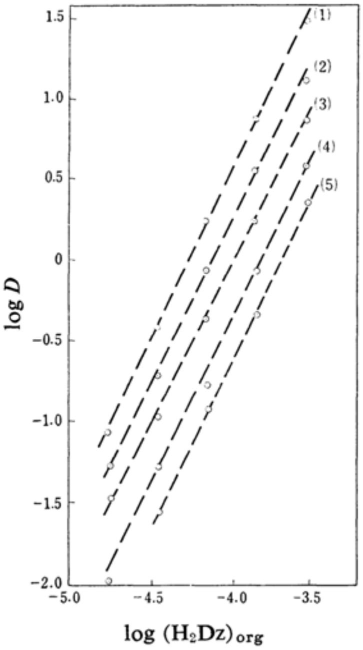

Fig. 2. Dependence of distribution ratio on the dithizone concentration.

$HClO_4$: (1) 0.10 M, (2) 0.23 M, (3) 0.55 M, (4) 1.31 M, (5) 3.12 M
Ionic strength: 3.12
Shaking temp.: 25°C
Shaking time: 30 min.
Slope of broken lines is 2.

The coordination number of the quadrivalent tellurium that appears in the solid compounds is 4 or 6. Although no data have been reported concerning its coordination number in solution, one may consider it not to exceed 6. If $N=4$, the extraction of tellurium with dithizone would not be possible, for in that case $p=0$. The only solution that satisfies Eqs. 1 and 2 is $N=6$, $\bar{p}=p=2$ and $\bar{m}=0$.

Therefore, the chemical species of tellurium extracted is supposed to be $Te(OH)_2(HDz)_2$* and the process of the extraction may be written as follows:

$$\begin{aligned} &Te(OH)_n{}^{(4-n)+}\ (aq.) + 2H_2Dz\ (org.) \\ &\quad = Te(OH)_2(HDz)_2\ (org.) + (4-n)H^+\ (aq.) \\ &\qquad + (n-2)H_2O\ (aq.) \end{aligned} \tag{3}$$

The distribution ratios of macro amounts of tellurium whose initial concentration in the aqueous layer is 4.25×10^{-5} M are shown in Fig. 3. Since, in the case of macro amounts, the concentration of dithizone at the extraction equilibrium differs from the initial concentration, the concentrations of dithizone were corrected on the assumption that the complex of dithizone contained two dithizonate anions to one tellurium cation. Plotting the logarithm of the distribution ratios against that of the concentrations of dithizone at equilibria, one could also obtain a straight line whose slope was 2 (Fig. 3).

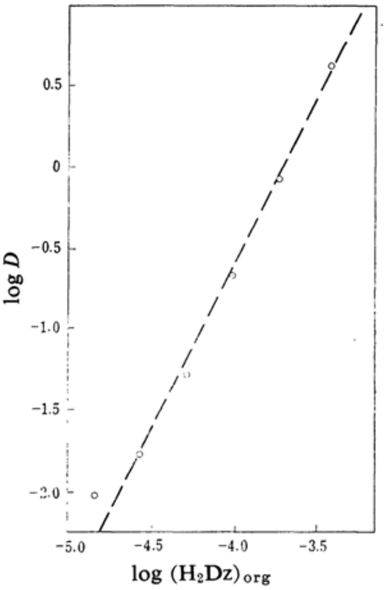

Fig. 3. Dependence of distribution ratio on the dithizone concentration.

Te(IV) before shaking: 4.25×10^{-5} M
$HClO_4$: 1.17 M
Shaking temp.: 20°C
Shaking time: 30 min.
Slope of broken line is 2.

The Tellurium Species in the Aqueous Layer.—In order to determine the species of tellurium in an acidic aqueous solution, the distribution ratio was measured as a function of the hydrogen ion concentration. The results are shown in Fig. 4, where log D is plotted against log (H^+).

The equilibrium quotients for Eq. 3 are represented as:

$$K_n = \frac{(Te(OH)_2(HDz)_2)_{org}(H^+)_{aq}{}^{(4-n)}(H_2O)_{aq}{}^{(n-2)}}{((Te(OH)_n)^{(4-n)+})_{aq}(H_2Dz)_{org}{}^2} \tag{4}$$

The distribution ratio is given by:

$$D = \frac{(Te(OH)_2(HDz)_2)_{org}}{\sum_n (Te(OH)_n{}^{(4-n)+})_{aq}} \tag{5}$$

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* $TeO(HDz)_2$ or $TeDz_2$ is also expected as the species of tellurium(IV) dithizonate. However, since $TeDz_2$ should be in the so-called "enol form,"[6] $TeDz_2$ may be excluded; because the "enol form" does not appear in other metal dithizonates extracted from a strongly acidic aqueous solution. At any rate, from this experiment, it is impossible to distinguish between $Te(OH)_2(HDz)_2$ and $TeO(HDz)_2$.

6) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York, London (1959), p. 140.

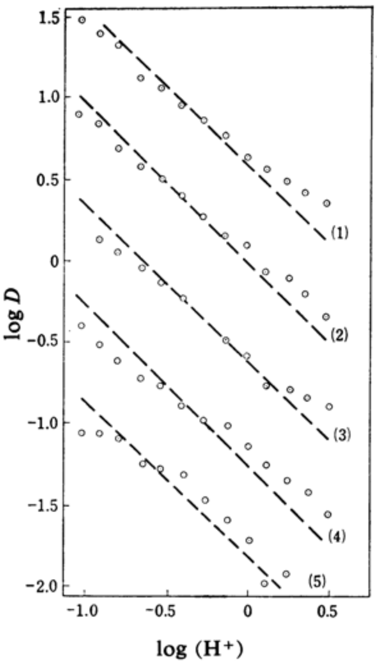

Fig. 4. Dependence of distribution ratio on the acid concentration.

H_2Dz in CCl_4: (1) 2.76×10^{-4} M, (2) 1.38×10^{-4} M, (3) 6.90×10^{-5} M, (4) 3.45×10^{-5} M, (5) 1.73×10^{-5} M
Ionic strength: 3.12
Shaking temp.: 25°C
Shaking time: 30 min.
Slope of broken lines is -1.

In this formulation the tellurium species containing dithizonate anions in the aqueous layer are neglected. This assumption may be valid under the present experimental conditions. Taking the partial derivative of $\log D$ with respect to $\log(H^+)$,

$$\partial \log D/\partial \log(H^+) = -4+f_1+2f_2+3f_3+4f_4+5f_5+6f_6 \qquad (6)$$

where;

$$f_n=\frac{(Te(OH)_n{}^{(4-n)+})}{(Te^{4+})+(Te(OH)^{3+})+\cdots+(Te(OH)_6{}^{2-})}$$

and

$$0\leqq f_n \leqq 1$$

By using Eq. 6 and the value of $\partial \log D/\partial \log(H^+)$ experimentally obtained, one can calculate the average number of hydroxyl groups attached to one tellurium atom. As can be seen from Fig. 4, $\partial \log D/\partial \log(H^+)$ is nearly -1, so f_3 is the predominant factor, corresponding to $Te(OH)_3{}^+$.

That tellurium(IV) exists as $Te(OH)_3{}^+$ in acid solutions (0.10—3.0 M) agrees with the results obtained from solubility[7,8] and ion-exchange studies[9]. Thus, the overall reaction of tellurium(IV) with dithizone in the extraction process may be written as follows:

$$Te(OH)_3{}^+(aq.)+2H_2Dz(org.)= Te(OH)_2(HDz)_2(org.)+H^+(aq.)+H_2O(aq.) \qquad (7)$$

The Effect of the Temperature on the Distribution Ratio.—In order to determine the effect of the temperature on the extraction, measurements of the distribution ratio of tellurium were made at 3, 10, 20, 30 and 40°C. The results are shown in Fig. 5.

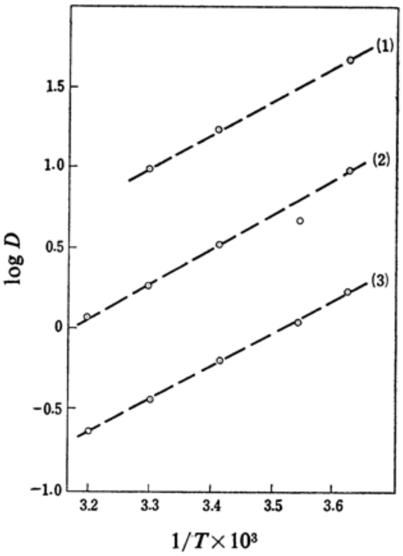

Fig. 5. Effect of temperature on the distribution ratio.

H_2Dz in CCl_4: (1) 5.80×10^{-4} M, (2) 2.54×10^{-4} M, (3) 1.27×10^{-4} M
Aqueous medium: $HClO_4$ 2.00 M
Shaking time: 30 min.

In general, for the equilibrium constant, K, of a reaction and the absolute temperature, T, the following thermodynamical relation holds:

$$(\partial \ln K/\partial(1/T))_p=-\Delta H^\circ/\boldsymbol{R} \qquad (8)$$

where $-\Delta H^\circ$ is the standard enthalpy change, $\boldsymbol{R}$ is the gas constant, and the subscript, p, implies that the pressure is constant.

The equilibrium constant, K, for Eq. 7 is written as follows:

$$K=\frac{[Te(OH)_2(HDz)_2][H^+]}{[Te(OH)_3{}^+][H_2Dz]^2} \qquad (9)$$

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[7] S. R. Schuhmann, *J. Am. Chem. Soc.*, **47**, 361 (1925).

[8] I. M. Issa and S. A. Awad, *J. Phys. Chem.*, **58**, 948 (1954).

[9] Y. Sasaki, *Japan Analyst* (*Bunseki-Kagaku*), **4**, 637 (1955).

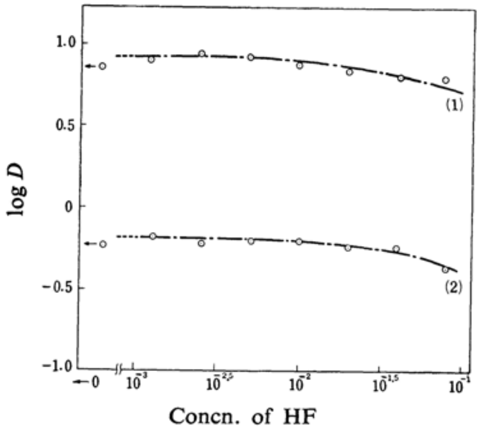

Fig. 6. Effect of fluoride on the distribution ratio.
H_2Dz in CCl_4: (1) 2.60×10^{-4} M, (2) 9.00×10^{-5} M
$HClO_4$: 2.00 M+NaF
Shaking temp.: 20°C
Shaking time: 50 min.

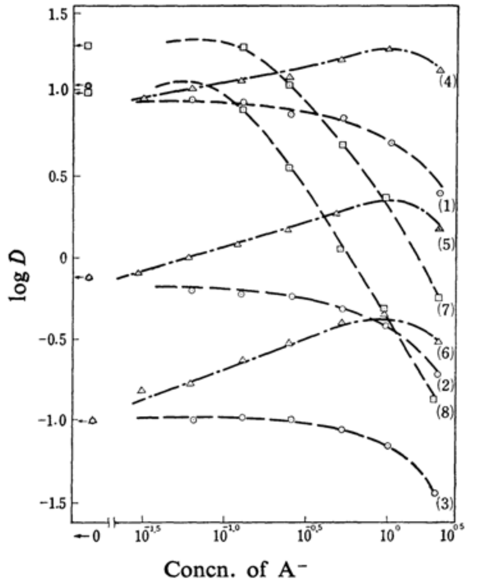

Fig. 7. Effect of chloride, bromide and iodide on the distribution ratio.
H_2Dz in CCl_4: (1) and (4) 3.39×10^{-4} M, (2) and (5) 9.00×10^{-5} M, (3) and (6) 4.50×10^{-5} M, (7) 5.70×10^{-4} M, (8) 2.89×10^{-4} M
(1), (2) and (3): chloride
(4), (5) and (6): bromide
(7) and (8): iodide
[H^+]: 2.00 M
Shaking temp.: 20°C
Shaking time: 50 min.
Ionic strength: 2.00

where the square brackets indicate the thermodynamical activity of the corresponding species. Equation 9 is rewritten as:

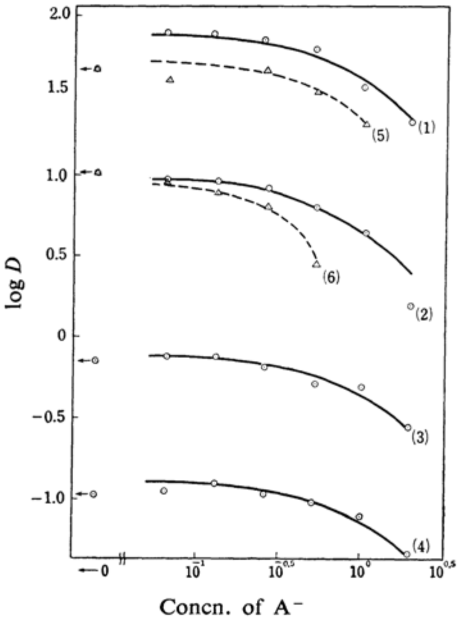

Fig. 8. Effect of bisulfate and nitrate on the distribution ratio.
H_2Dz in CCl_4: (1) and (5)* 7.78×10^{-4} M, (2) and (6)* 3.39×10^{-4} M, (3) 9.00×10^{-5} M, (4) 4.50×10^{-5} M
(1), (2), (3) and (4): bisulfate
(5) and (6): nitrate
[H^+]: 2.00 M
Shaking temp.: 20°C
Shaking time: 50 min.
Ionic strength: 2.00
* After shaking dithizone was partially oxidized by nitric acid.

$$K=D\times\gamma_2\times\gamma_H\times(H^+)/\gamma_1\times\gamma_D{}^2\times(H_2Dz)^2 \quad (10)$$

where γ_1, γ_2, γ_H and γ_D are the activity coefficients of the tellurium(IV) ion, tellurium dithizonate, the hydrogen ion and dithizone respectively. Since the concentration of the solutes in the organic layer is very low, both γ_2 and γ_D could be regarded as unity. When one assumes that the temperature dependence of the ratio, γ_H/γ_1, is very small, one can take the following formulation:

$$(\partial \ln K/\partial(1/T))_p \cong (\partial \ln D/\partial(1/T))_p \quad (11)$$

Thus, by plotting log D vs. $1/T$, one can obtain straight lines. From the slope of the lines in Fig. 5, the enthalpy change, $\Delta H°$, may be roughly estimated to be −10.4 kcal./mol.

The Effect of Various Anions on the Distribution Ratio. — Figures 6, 7 and 8 show the effects of fluoride, chloride, bromide, iodide, bisulfate and nitrate on the distribution ratios of tellurium(IV). In each case, the ionic strength was kept constant with perchloric acid. In the experiments involving fluoride, the extraction was carried out in glass tubes

TABLE I. EFFECT OF VARIOUS ACIDS ON THE EXTRACTION

Substance	Concn. M	$(D_x/D_0)\times100$*1 (1)	(2)
Formic acid	1.0	100	100
Acetic acid	1.0	100	100
Oxalic acid	0.01	86	94
Malonic acid	0.01	85	94
Succinic acid	0.01	92	87
Fumaric acid	0.05	100	100
Maleic acid	0.05	84	86
Citric acid	0.01	87	84
Tartaric acid	0.01	93	97
Orthophosphoric acid	0.5	95	92
Orthoboric acid	0.1	97	99
Metasilicic acid	0.01	91	95
NTA*2	0.01	100	100
EDTA	0.01	93	94
CyDTA*3	0.01	100	92
DTPA*4	0.01	99	100
GEDTA*5	0.01	91	100

*1 Extracted with (1) 3.39×10^{-5} M, (2) 9.00×10^{-5} M H_2Dz in CCl_4
D_0: Distribution ratio of Te(IV) when extracted from 2.00 M $HClO_4$.
D_x: Distribution ratio of Te(IV) when extracted from 2.00 M $HClO_4$ + a corresponding acid.
*2 NTA: Nitrilotriacetic acid
*3 CyDTA: 1,2-cyclohexanediaminetetraacetic acid
*4 DTPA: Diethylenetriaminepentaacetic acid
*5 GEDTA: Glycoletherdiaminetetraacetic acid
Shaking temp.: 20°C
Shaking time: 50 min.

the insides of which were coated with "Silicone."*

Another series of experiments extracting tellurium by dithizone were carried out in the presence of various acids, including phosphoric acid, boric acid, silicic acid and several organic acids. The results are shown in Table I.

The Absorption Spectrum and the Molar Extinction Coefficient of Tellurium Dithizonate in Carbon Tetrachloride.—Four milliliters of perchloric, sulfuric, hydrochloric or nitric acid solutions of tellurium(IV) were shaken with 4 ml. of a freshly-purified dithizone carbon tetrachloride solution. An aliquot of the organic layer was then diluted with carbon tetrachloride and subjected to the spectrophotometric measurement.

In all these cases, one could not obtain a pure tellurium dithizonate solution, only a mixture of dithizone and tellurium dithizonate. For example, the absorption spectrum for the extract from sulfuric acid is shown in Fig. 9. Assuming that the absorption peak at 620 mμ is wholly due to dithizone, one can analyze the curve into two components and assign the maximum absorption of tellurium dithizonate at 427 mμ, as Fig. 9 shows.

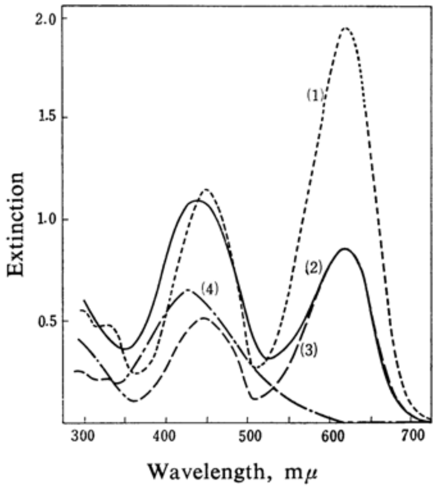

Fig. 9. Absorption spectra of dithizone and tellurium dithizonate in carbon tetrachloride.
----- (1): Absorption spectrum of dithizone (5.66×10^{-5} M)
——— (2): Absorption spectrum of a mixture of tellurium dithizonate (1.58×10^{-5} M) and dithizone (2.50×10^{-5} M)
— — — (3): Assumed absorption spectrum of dithizone in (2)
— - — (4): Resulting absorption spectrum of tellurium dithizonate in (2), that is: (2) − (3).

TABLE II. MOLAR EXTINCTION COEFFICIENT OF TELLURIUM DITHIZONATE IN CARBON TETRACHLORIDE

Aqueous medium	concn. M	Initial concn. of Te(IV) M	$\varepsilon_{427\,m\mu}$ $M^{-1}\,cm^{-1}$
$HClO_4$	1.90	9.77×10^{-5}	4.13×10^4
H_2SO_4	0.692	4.88×10^{-3}	4.12×10^4
	0.433	1.63×10^{-3}	4.17×10^4
HCl	1.07	8.02×10^{-3}	4.03×10^4
	0.230	3.76×10^{-4}	4.07×10^4
HNO_3	0.814	8.34×10^{-4}	3.90×10^4

The molar extinction coefficients at 427 mμ were calculated for several extracts; they are tabulated in Table II. Since the wavelengths of the maximum absorption and the molar extinction coefficients are equal for all these extracts within the range of experimental error, they are supposed to be identical entities.

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* Polone T, made by Shin-etsu Kagaku Co., Ltd., Japan.

Summary

Tellurium(IV) can be extracted into organic layers with dithizone. The analysis of the experimental results suggests, as the main process of extraction:

$$\begin{aligned}&\mathrm{Te(OH)_3^+}\ (\text{or } \mathrm{TeOOH^+})\ (\text{aq.}) + 2\mathrm{H_2Dz}\ (\text{org.})\\ &\quad = \mathrm{Te(OH)_2(HDz)_2}\ (\text{or } \mathrm{TeO(HDz)_2})\ (\text{org.})\\ &\qquad + \mathrm{H^+}\ (\text{aq.}) + x\mathrm{H_2O}\ (\text{aq.})\end{aligned}$$

The spectrophotometric measurements show that tellurium dithizonate in carbon tetrachloride has an absorption maximum at 427 mμ, where the molar extinction coefficient is $4.10 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$.

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