BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 817—821 (1967)

Solvent Extraction and Spectrophotometric Determination of the Pertechnetate Ion with Methyl Violet

Taitiro FUJINAGA, Mutsuo KOYAMA, Yoshihiko KANCHIKU*[1] and Shigeo TSURUBO
Chemistry Institute, Faculy of Science, Kyoto University, Sakyo-ku, Kyoto

(Received August 10, 1966)

A spectrophotometric method of determination of TcO_4^- subesquent to solvent extraction with methyl violet was investigated. Methyl violet which has a molar extinction coefficient of about 2×10^5 at 585 mμ in a neutral aqueous solution was found to be extractable with TcO_4^- into monochlorobenzene. The absorption maximum of the dye in the organic layer after extraction shifts to 595 mμ, at which point the absorbance is proportional to the amount of TcO_4^- added to the aqueous solution. The effect of the pH on the absorbance of organic layer was very small as long as the absorbance was measured against the reagent blank as a reference. Over the wide range of pH values from 2 to 10, an approximately constant absorbance was obtained for a fixed amount of TcO_4^-. Effects of diverse ions were also examined. Alkali salts of phosphate, borate, citrate, and tartrate have little effect on the absorbance of the organic layer, whereas perchlorate and perrhenate seriously interfere. When the extraction efficiencies of TcO_4^- were measured using ^{95m}Tc and ^{97m}Tc as tracers, they were found to be quantitative, even at a concentration as low as 10^{-12} M.

The chemistry of technetium has mainly been studied using a minute quantity produced by the irradiation of molybdenum with either charged particles or neutrons. Macro amounts of technetium have, however, become available in recent years, and so now it is possible to separate and to determine the element in a manner similar to that usually used. Generally, gravimetry as with metallic technetium¹⁾ or tetraphenylarsonium pertechnetate²⁾ has been used for the determination of macro amounts of technetium. Several spectrophotometric procedures to determine technetium

---

[1] Present address; Mitsubishi Rayon Research Institute, Otake, Hiroshima.

1) J. W. Cobble, "Treatise on Analytical Chemistry," Part II, Section A, ed. by I. M. Kolthoff *et al.*, John Wiley & Sons, Inc., New York (1963), p. 424.
2) *Ibid.*, p. 426.

have also been investigated, using color development with reagents such as thioglycolic acid,³⁾ toluene dithiol,⁴⁾ diphenylcarbazide,⁵⁾ and thiocyanate.⁶⁾ The methods using the former two reagents are not sensitive, however, and the color developments of technetium with the latter two are said to lack stability. Recently, analytical methods have been extensively developed to determine colorless anions, such as perchlorate,⁷⁾ perrhenate,⁸,⁹⁾ nitrate¹⁰⁾; these methods apply, that is, to the extraction of anions with large cationic chelates or dyestuffs which have large absorptions in the visual spectral region.

In the present paper, a similar method will be applied to the determination of the pertechnetate ion by extracting it into monochlorobenzene, using methyl violet as the counter ion. This method has a high sensitivity and fairly good separation from such anions as sulfate, phosphate, chloride, and some of the organic acids. Since perchlorate and perrhenate ions behave similarly to the pertechnetate ion, an appropriate separation is needed before extraction.

Experimental

Reagents. *Standard Solution of Technetium.* An aqueous solution of ammonium pertechnetate obtained from the Oak Ridge National Laboratory was diluted to 1.02 mg ^{99}Tc/m*l*. This solution was then standardized by precipitating and weighing tetraphenylarsonium pertechnetate according to the standard method for rhenium.¹¹⁾ The spectra in the ultraviolet region were also examined; no impurity was detected. Separately, ^{95m}Tc and ^{97m}Tc were also prepared with a cyclotron by bombarding molybdenum with 20 MeV deutrons and isolated as pertechnetate solution.¹²⁾

Methyl Violet Solution. Methyl violet chloride salt was dissolved in water and shaken with the organic solvents before use in order to remove any extractable impurities. The concentration of the solution was 10^{-3} M. The other chemicals were of reagent grade unless otherwise stated.

Apparatus. A Shimadzu automatic recording spectrophotometer, SV 50 A, was used for the measurement of the absorption spectra. For the quantitative measurement, a Shimadzu manual spectrophotometer, QR 50, was used. Absorption cells with a path length of 1 cm were employed. pH measurements were peroformed with a Hitachi-Horiba model P pH meter. The radioactivity of ^{99}Tc was measured with an Osaka Dempa G. M. counter, the window thickness of which was 1.5 mg/cm². Gamma ray counting was carried out with a Nuclear Data 512-channel pulse-height analyser equipped with a 2×1 1/2 inch well-type crystal.

Procedure. The volume of the aqueous layers was kept at 20 m*l* and that of the organic layers at 10 m*l* throughout the extraction experiments. Methyl violet, buffer, and pertechnetate solutions were added in that order to a 50 m*l* separatory funnel; the aqueous phase was finally diluted to 20 m*l* with the addition of water.

After 10 m*l* of organic solvents had been poured in, the funnel was shaken for 5 to 15 min. The two phases had clearly separated within several minutes after the end of shaking. The organic layer was dried with anhydrous sodium sulfate and then transferred to an absorption cell. The absorbance was measured against the organic solvents used.

The extractant was diluted with the organic solvents, if necessary, in order to obtain a high precision.

Results and Discussion

Absorption Spectra. The absorption spectra of methyl violet in an aqueous solution and in monochlorobenzene are compared in Fig. 1. In a neutral aqueous solution, methyl violet has an absorption maximum at 585 mμ, while the absorption spectrum of that portion which was extracted in monochlorobenzene exhibited a slight red shift and an absorption maximum appearing at 595 mμ.

Methyl violet is slightly extracted into the organic layer in the absence of technetium(VII), from aqueous solutions buffered with phosphates. This fact offers a basis for the determination of technetium.

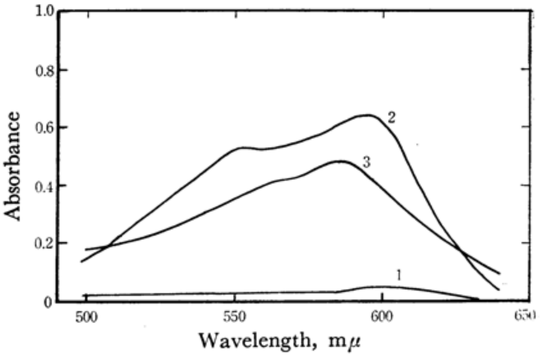

Fig. 1. Absorption spectra of methyl violet.

1. Methyl violet extracted into monochlorobenzene in the absence of TcO_4^-
2. Methyl violet extracted with TcO_4^- into monochlorobenzene
3. Methyl violet in phosphate buffer solution; pH 6.9

---

3) F. J. Miller and P. F. Thomason, *Anal. Chem.*, **34**, 530 (1962).

4) R. J. Meyer, R. D. Oldham and R. P. Larsen, *ibid.*, **36**, 1975 (1964).

5) F. J. Miller and H. E. Zittel, *ibid.*, **35** 299 (1963).

6) C. E. Crouthamel, *ibid.*, **29**, 1756 (1957).

7) Y. Yamamoto and K. Kotsuji, This Bulletin, **37**, 785 (1964).

8) I. Iwasaki, S. Utsumi and C. Kang, *ibid.*, **36**, 325 (1963).

9) I. A. Blyum and T. K. Dushima, *Zavodsk. Lab.*, **28**, 903 (1962).

10) Y. Yamamoto, S. Uchikawa and K. Akabori, This Bulletin, **37**, 1718 (1964).

11) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

12) M. Ishibashi, T. Fujinaga and M. Koyama, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)* **81**, 1260 (1960).

TABLE 1. EFFECTS OF ORGANIC SOLVENTS AND TIMES OF EXTRACTION ON THE RECOVERY OF TECHNETIUM

Organic solvent	Time of extraction and percent recovery				
	1 %	2 %	3 %	4 %	5 %
Monochlorobenzene	100.0 100.0				
n-Butylacetate	56.1 56.1	80.7 76.7	90.5 81.5	95.3 82.3	98.4
Isobutylacetate	41.0 41.0	65.2 59.2	79.5 67.7	87.9 71.4	92.9 73.2
Toluene	10.0 10.0	19.0 15.7	27.1 18.1	34.4	41.0

Organic layer	10 *ml*, Initial TcO_4^- concn. 1.02 10^{-5} M
Aqueous layer	20 m*l*, Initial methyl violet concn. 5×10^{-4} M
pH	5.9, Buffered with phosphate

TABLE 2. RECOVERY OF TECHNETIUM(VII)

Sample No.	^{95m}Tc and ^{97m}Tc in aqueous phase		^{95m}Tc and ^{97m}Tc in organic phase	
	net cpm	%	net cpm	%
1	15 ±2.2	0.38±0.06	3906±36	99.62±0.92
2	14.2±2.1	0.37±0.05	3855±36	99.63±0.92

Organic Solvents and Extraction Efficiencies. Several kinds of organic solvents were tested in order to achieve a quantitative extraction of technetium. In alcohols and in ketones, methyl violet is extracted even in the absence of technetium and so can not be used for the present purpose. In nonpolar solvents, such as benzene, cyclohexane, and carbon tetrachloride, the dye can not be extracted under any conditions. In Table 1, the esters, toluene and monochlorobenzene are compared with regard to the extractability of methyl violet with technetium. It can be seen that the quantitative extraction of technetium can be achieved only by using monochlorobenzene as the organic solvent.

The extraction percentages were also determined by using ^{95m}Tc and ^{97m}Tc, the concentration of which were estimated to be as low as 10^{-12} M. One milliliter each of both phases was taken into a test tube after extraction, and the radioactivities of gamma rays with energies larger than 0.584 MeV were counted with a 512-channel pulse-height analyser. The results are shown in Table 2. It is obvious that the quantitative extraction of technetium(VII) can be performed using this procedure.

pH Dependence of the Extraction. To establish the optimum pH value of the aqueous phase for the extraction of technetium, the dependence of the absorbance of the organic layer on the pH values was studied. The aqueous layer turns greenish below pH 3 and yellowish above pH 9. The spectra of the extracted species, however, are quite similar over the wide pH range studied.

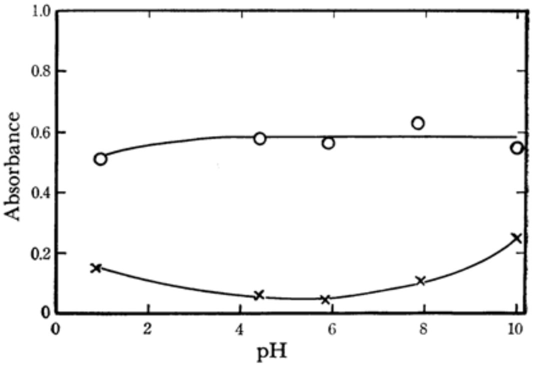

Fig. 2. Effects of pH on the extraction of TcO_4^-.
-○- 2.5×10^{-6} M TcO_4^-; Absorbance was measured against reagent blank.
-×- Reagent blank; Absorbance was measured against monochlorobenzene.

In Fig. 2, the absorbance of the organic layers measured at 595 mμ are plotted against the pH values of aqueous solutions. Although the absorbance of the organic layers increases with an increase in the pH values of the aqueous solution when the concentrations of technetium and methyl violet are kept constant, a nearly constant absorbance is obtained over the pH range from 3 to 10 if the absorbance of the samples is measured against the reagent blank at each pH.

Concentration of Methyl Violet. The effect of the concentration of methyl violet on the absorbance of the organic layer was examined. The

TABLE 3. EFFECTS OF DIVERSE IONS ON THE EXTRACTION OF TECHNETIUM

Diverse ion	Concn., M	Abs.	Diverse ion	Concn., M	Abs.
none	none	0.281	$B_4O_7^{2-}$	1×10^{-2}	0.306
ClO_3^-	1×10^{-5}	0.426	MnO_4	1×10^{-5}	0.254
	1×10^{-6}	0.271	MoO_4^{2-}	1.5×10^{-4}	1.31
Cl^-	1×10^{-3}	0.331	WO_4^{2-}	1.5×10^{-6}	0.298
	1×10^{-5}	0.283		1×10^{-5}	0.184
Br^-	1×10^{-6}	0.279	CH_3COO^-	1×10^{-1}	0.317
I^-	1×10^{-6}	0.324	Tartrate	1×10^{-3}	0.296
SCN^-	1×10^{-6}	0.611	Citrate	1×10^{-1}	0.405
NO_3^-	1×10^{-6}	0.285	Hydroxylamine	1×10^{-2}	0.276
SO_4^{2-}	1×10^{-1}	0.288	Hydrazine	1×10^{-2}	0.285
SO_3^{2-}	1×10^{-3}	0.000			

Concentration of TcO_4^-: 1.30×10^{-6} M, Absorbance at 595 mμ

results show that more than 2×10^{-5} M of methyl violet is required for less than 10^{-5} M of technetium in order to obtain a quantitaitve extraction. In the present study, the methyl violet concentration was therefore kept at 5×10^{-4} M throughout the experiments.

Concentration of the Buffer Solution. As shown in Fig. 3, little influence of the concentration of the buffer salt is observed upon the absorbance of the organic layer as long as the phosphate ion is employed as a buffering agent.

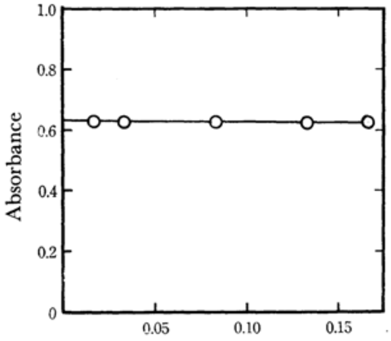

Fig. 3. Effects of the concentration of buffer solution on the extraction of TcO_4^-.
Buffer: phosphate, pH 5.9

Calibration Curve. A calibration curve was made by extracting different amount of technetium with methyl violet into 10 m*l* portion monochlorobenzene from 20-m*l* portions of aqueous solutions, the composition of which was 5×10^{-4} M in methyl violet and 0.05 M in phosphate buffer respectively at pH 5.9. The absorbance at 595 mμ of the extract was measured against a blank treated in the same way as the samples except that no technetium was added. In cases where the absorbance of the organic layer was more than 0.8, the organic layer was diluted with monochlorobenzene to such an extent that precise measurements could be carried out.

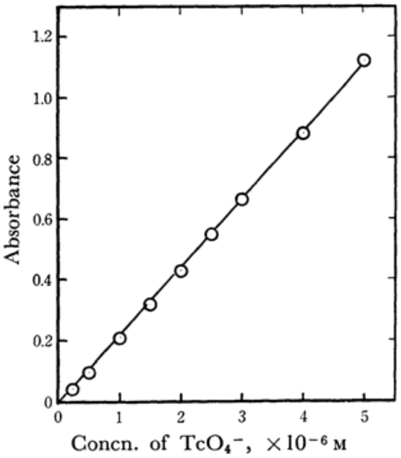

Fig. 4. Calibration curve of TcO_4^-.
Volume of aqueous phase: 20 m*l*; Volume of organic phase: 20 ml
Concentration of methyl violet: 2×10^{-4} M
Concentration of phosphate buffer: 0.1M, pH 5.9

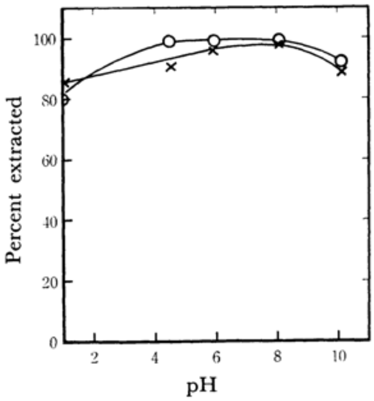

Fig. 5. Effects of pH on the extraction of ReO_4^- and ClO_4^-.
-○- ReO_4^-; -×- ClO_4^-
Concentration of methylviolet; 2×10^{-4} M
Concentration of ReO_4^- and ClO_4^-; 2.5×10^{-6} M

A good linear relationship was obtained by plotting the absorbance of organic layers against the concentration of technetium added in the aqueous phase, as Fig. 4.

Influence of Diverse Ions. Mainly the influence of the diverse anions on the absorbance was examined using experimental conditions similar to those used in the calibration curve preparation. Among anions, perchlorate and perrhenate ions have such a similar structure to that of the pertechnetate ion that the pH dependence on their extraction was examined especially, as is shown in Fig. 5.

Table 3 illustrates the degree of interference of diverse ions added to a solution containing 1.30×10^{-6} M of technetium(VII). Hydrazine and hydroxylamine were tested because they might reduce technetium(VII) to a lower oxidation state under the given conditions.

No appreciable interference was detected, however. Most of the cations except alkaline metal ions cause trouble by forming precipitates with the phosphate ion which are eventually suspended between the organic and aqueous layers.

However, the interference of cations can be eliminated by some preliminary treatment, for example, passing the sample through a column of cation-exchange resin before the extraction.

The authors' thanks are due to Professor Y. Uemura and the members of the cycrotron crew of the Kyoto University for giving them an opportunity to produce ^{95m}Tc and ^{97m}Tc.

This work was partly supported by Scientific Research Grant of the Ministry of Education No. 4056, for this the authors are grateful.