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Extraction-spectrophotometric Study of the System Technetium-Chromotropic Acid-Long Chain Quaternary Ammonium Salt

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A simple and highly selective extraction-spectrophotometric determination of technetium is described. The ion-associate formed between the technetium-chromotropic acid (CA) anion and trioctylmethylammonium (TOMA) is extracted with toluene in acidic media. The absorption maximum of the extracted species occurs at 630 nm, the molar absorptivity being $3.1\times10^3\,dm^3\,mol^{-1}\,cm^{-1}$. The composition of the ion-associate is estimated to be $[Tc(CA)_2(TOMA)_3]$.

Radiochemical methods are the most widely used procedures so far for technetium determination. These methods, however, require extensive chemical separation and purification to remove interferences and this can be difficult and laborious. The recent increase in technetium production has aroused interest in the development of methods of analysis that could be used to supplement the radiochemical ones. Methods described so far for technetium determination by means of nonradiochemical processes are however very scarce.[1] On the other hand, the recent production of appreciable quantities of technetium has allowed initiation of the study of its chemical behavior,[2] that has been restricted for a long time due to available quantities of this element being very small. In this aspect it can be pointed out that, although some complexes of the element were isolated for its different states of oxidation and even in some cases its structure was determined, knowledge of the behavior of this element in solution is still unknown in many aspects.

The present paper is concerned with the spectrophotometric determination of traces of technetium by extracting its complex with chromotropic acid in the presence of Adogen 464. The absorbance of the organic phase is very stable and is thus suitable for routine work. This system seems worthwhile because of the simplicity and high selectivity of the procedure.

Experimental

Reagents and Apparatus. Stock solution of chromotropic acid (CA) (supplied by Panreac) included a 7.5 $g\,dm^{-3}$ aqueous solution of the compound ($C_{10}H_8O_8S_2\cdot 2H_2O$). Trioctylmethylammonium chloride (TOMA), better known as Adogen 464 (supplied by Serva) included a 2.5 $g\,dm^{-3}$ solution in toluene.

Technetium-99 in solution form, as ammonium pertechnetate, was obtained from Amersham/Searle Co., Arlington Heights, Ill. A technetium solution of 119 ppm was prepared by dilution of the primary standard with water.

A Perkin-Elmer 552 spectrophotometer with 1.0-cm cells was used.

Extraction Procedure. To a series of 100 cm^3 separatory funnels, add 5 cm^3 of chromotropic acid (7.5 $g\,dm^{-3}$), 2 cm^3 of 18% L-ascorbic acid, 2.5 cm^3 of concentrated HCl (11.8 $mol\,dm^{-3}$), and the volume of technetium solution necessary for the final concentration to be between 0.5—6 ppm, and dilute to 25 ml with water. Mix well, and warm in a steam bath for 10 min. Add 5 ml of Adogen 464 (2.5 $g\,dm^{-3}$) and shake on a mechanical shaking apparatus for 30 min. Allow to stand for adequate time to separate the layers and discard the aqueous layer. Measure the absorbance of the organic layer at 630 nm using toluene as a reference.

Results and Discussion

Absorption Spectra. Maximum absorption of the

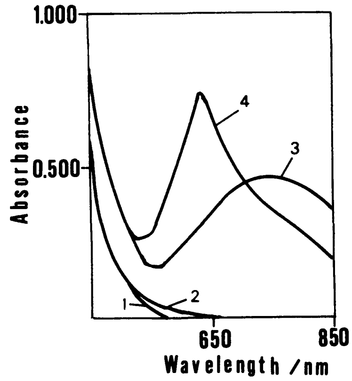

Fig. 1. Absorption spectra for Tc–CA complex. $[CA]=4.4\times10^{-3}\,mol\,dm^{-3}$, [Ascorbic acid]=0.1 $mol\,dm^{-3}$, [Tc]=23.8 ppm, $[TOMA]_{org}=6\times10^{-3}\,mol\,dm^{-3}$. 1: Reagent blank in aqueous solution, 2: Reagent blank in toluene phase, 3: Complex Tc–CA in aqueous solution, 4: Ion pair Tc–CA–TOMA in toluene phase. The extraction was carried out using 5 cm^3 of aqueous phase and 5 cm^3 of toluene phase.

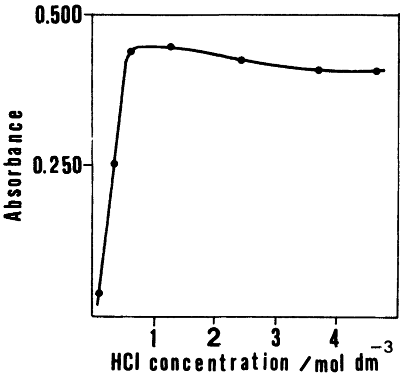

Fig. 2. Absorbance at 740 nm *versus* HCl concentration.
$[CA]=4.4\times10^{-3}\,mol\,dm^{-3}$, [Ascorbic acid]=0.1 $mol\,dm^{-3}$, [Tc]=23 ppm.

TABLE 1. CHARACTERISTICS OF THE PHOTOMETRIC METHODS FOR TECHNETIUM DETERMINATION

Reagent	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	Main interferences	Ref.
1,5-Diphenylcarbazide	520	48600	Fe(III), Cr(VI), Ce(IV)	4
Thiocyanate	510	47500	U(VI), Fe(III), Mo(VI)	5
Mercaptoacetic acid	655	1800	Mo(VI), Cr(VI), Ru(VII), U(VI), Fe(III)	6
3,4-Toluenedithiol	450	15000	Mo(VI), Cr(VI), Ru(VII)	7
Thiocyanate	585	16500	Fe(III), Mo(VI)	8
Thiocyanate	510	50000	Fe(III), Mo(VI)	8

Tc–CA complex in aqueous media occurs at 740 nm (ε=2.0×10^3 dm^3 mol^{-1}cm^{-1}), as can be seen in Fig. 1. The absorption spectrum (Fig. 1) of the extracted ternary system shows important changes of absorptivity and the maximum position (λ_{max}=630 nm, ε=3.1×10^3 dm^3 mol^{-1}cm^{-1}) as a result of the ion-associate formation and extraction (the band shift involved is about 110 nm).

Effect of the Variables. The effect of pH on the formation of the Tc–CA complex was investigated. It was deduced from this study that complex formation is detected only when the assay takes place in acid medium as can be seen in Fig. 2. Maximal absorbance corresponds to hydrochloric acid interval concentrations of 0.6—1.4 mol dm^{-3}. At higher concentration, the absorbance decreases slightly, probably as a consequence of complex destruction. At lower hydrochloric acid concentrations, the absorbance decreases markedly. Formation of the Tc–CA complex only in strong acid medium can be explained admitting that the reduction process of Tc(VII) is more favored in this medium and not as a consequence of instability of complex species formed at lower hydrochloric acid concentrations. Thus, it has been proved that once having obtained the colored species in 1.2 mol dm^{-3} hydrochloric acid, they are not destroyed until pH=5 when basifying.

Ascorbic acid is used to reduce Tc(VII), the most stable species of the element in aqueous solution, to Tc(V), the probable oxidation state required for the CA color development. Other reductants produced either no color, or not as much color as ascorbic acid. Thus, tin(II) chloride seems. to be too strong and in the presence of a little excess of this reductant, absorbance decreases notably. The color does not develop in the absence of this special reductant because the CA is unable to act as a reductant by itself. The color appearance is not instantaneous and is favored by means of calefaction. It has been proved that for maximum color development, 10 min calefaction in a steam bath is necessary. A final concentration of 0.5% ascorbic acid is sufficient for maximum color development.

The effects of changing the CA and TOMA concentrations on the absorbance of the ternary complex were examined. The absorbance was found to increase rapidly on addition of CA up to a technetium:CA mole ratio of 1:12, when higher than this value it was practically independent of reagent concentration. For TOMA, this ratio was 1:8. It should be remembered that a very large excess of surfactant can retard the rate at which the phases separate and remain clear.$^{3)}$ The stability of the ternary complex was studied. The absorbance of the extracted phase was stable at least for 24 h.

Nature of the Ion-associate. To determine the composition of the formed species, the Yoe-Jones method was used. Thus, stoichiometries of 1:2 (Tc:CA) and 1:2:3 (Tc:CA:TOMA) were found, suggesting that the extracted species is an ion-associate with formula Tc(CA)$_2$(TOMA)$_3$. This is in good agreement with the hypothesis that suggests the V oxidation state for technetium.

Characteristics of the Analytical Method. When the recommended procedure was used, Beer's law was followed in the range 0.5—6 μg Tc cm^{-3}. The molar absorptivity and precision of the method were established by carrying out ten parallel experiments. The molar absorptivity thus obtained is 3.1×10^3 dm^3 mol^{-1} cm^{-1}, which corresponds to a Sandell sensitivity of 31.9 ng Tc cm^{-2} for A=0.001. The relative standard deviation was 1.3% (95% confidence).

The selectivity of the method was tested by application of the recommended procedure in the presence of several foreign ions. A 100-fold amount of each of Ca, Sr, Ba, Mg, Ag, Ni, Co(II), Zn, Mn(II), Pb, Al, Cr(III), Fe(III), Mo(VI), W(VI), U(VI), Re(VII), V(V), NO_3^-, and SO_4^{2-} did not interfere. Only Cu(II) causes some serious interference. Thus, the presence of Cu(II) in large amounts prevents complex formation. Only 0.5 ppm of Cu(II) is tolerated. It is important to point out that U(VI), Re(VII), W(VI), and Mo(VI) which frequently accompany technetium and cause important disturbances in most of nonradiochemical procedures for technetium determination, do not cause any interference. This selectivity compares favorably with those obtained for other technetium complexes used spectrophotometrically (Table 1).

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