Chelate Formation between Thorium(IV) and Sulfodichlorohydroxydimethylfuchson Dicarboxylic Acid (Trisodium Salt). Studies on the Composition and Stability of the Chelate and Analytical Applications of the Reaction

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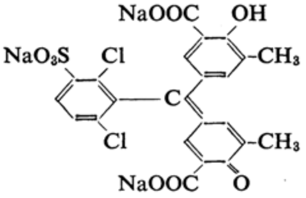
Several members of the dyes of the hydroxytriphenylmethane group are known to form characteristic colored products with inorganic ions in solution, and due to this property, they are used variously as metallo-chromic indicators in complexometric titrations, as colorimetric reagents for detection and determination of microamounts of metals and as spot reagents.

One of the important members of this group of dyes is sulfodichlorohydroxydimethylfuchson dicarboxylic acid (trisodium salt, commonly known as Chrome Azurol S and abbreviated here as CAS; Color Index 723) represented by the following structure:



The main use of the reagent, hitherto, has been as a metallochromic indicator in complexometric titrations due to its tendency of forming characteristic colored chelates in solution with certain metal ions. It has been used by Willard and Horton[1] as an indicator in the titration of fluoride with thorium. Theis, and Musil and Theis[2] employed the reagent in the chelatometric determination of aluminum, copper and zinc, and for detecting beryllium in weakly acidic solutions. The utility of Chrome Azurol S as an indicator for zirconium was examined by Fritz and Fulda[3] who found it not to be satisfactory. Under varied specific conditions, Malát and Tenérova[4] used the reagent as an indicator for the complexometric determination of nickel, cerium and lanthanum. The simultaneous determination of iron(III) and aluminum(III) by EDTA titration using Chrome Azurol S as an indicator has also been described by Matsuo[5]. Sangal and Dey[6] have carried out the complexometric determination of thorium using Chrome Azurol S as an indicator.

Few applications of the reagent, except for its use in the determination of fluoride by the bleaching of its colored lakes with metals have been reported in the realm of colorimetric analysis. Ravinson and Harley[7] suggested the spectrophotometric determination of fluoride ion, which prevents the color development of the thorium-Chrome Azurol S lake. Macnulty and Woolard[8] described the use of an aluminum Chrome Azurol S chelate for the micro-determination of fluoride, and also Silverman and Shideler[9] made studies on the spectrophotometric determination of beryllium and fluoride with the reagent.

In view of the interesting chromophoric reactions of Chrome Azurol S, the present investigations were undertaken. It was observed to form very stable colored chelates in aqueous solution with copper(II), beryllium(II), magnesium(II), cadmium(II), aluminum(III), lanthanum(III), cerium(IV), titanium(IV), zirconium(IV), lead(II), thorium(IV), molybdenum(VI), uranium(VI), iron(III), cobalt(II), nickel(II), and palladium(II) under specific experimental conditions. This communication records the investigations with the thorium(IV)-chelate. The composition and stability have been determined by two different methods using absorbance measurements, and the results further corroborated by performing electrical conductance studies.

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1) H. H. Willard and C. A. Horton, *Anal. Chem.*, **22**, 1190 (1950).

2) M. Theis, *Z. anal. Chem.*, **144**, 106, 192, 275 (1955); A. Musil and M. Theis, ibid., **144**, 427 (1955).

3) J. S. Fritz and M. O. Fulda, *Anal. Chem.*, **26**, 1206 (1954).

4) M. Malát and M. Tenérova, *Chem. Listy*, **51**(11), 2135 (1957).

5) T. Matsuo, *Bunseki Kagaku*, **7**, 557 (1958).

6) S. P. Sangal and A. K. Dey, *Z. anal. Chem.*, **178**, 415 (1961).

7) D. Ravinson and J. H. Harley, *Anal. Chem.*, **25**, 795 (1953).

8) B. J. Macnulty and L. D. Woolard, *Anal. Chim. Acta*, **14**, 452 (1956).

9) L. Silverman and M. E. Shideler, U. S. At. Energy Comm. NAA-SR-2686, pp. 21 (1958), *Anal. Chem.*, **31**, 152 (1959).

Experimental

Materials. — *Standara Thorium Solution.* — BDH (AnalaR) sample of thorium chloride was dissolved in double distilled carbon dioxide-free water. The metal was estimated as oxalate in 4% hydrochloric acid and weighed as thorium(IV) oxide after ignition. A 0.1 M stock solution was prepared.

Reagent Solution.—BDH indicator Chrome Azurol S (trisodium salt; Color Index 723) was employed for making the solutions, which were standardized by determining the sulfur content of the compound. Double distilled carbon dioxide-free water was used and always fresh solutions were prepared.

Solutions of Diverse Ions.—These were prepared by dissolving the respective compounds (all reagent grade) in distilled water and made to suitable strengths.

Protective Colloid.—A 0.1% solution of dextrin was prepared in distilled water and filtered. Suitable amounts of this solution were added to the mixtures to avoid any chances of the precipitating out of the lake, as such a tendency was observed at certain concentrations. It was found that although dextrin slowly loses its protective properties with the passing of time, yet, it is by far, the most suitable reagent for the present purpose.

Other Reagents.—All other reagents were of analytical grade and were used without further purification.

Instruments Procedure and Calculations.—*Absorbance Measurements.*—A Unicam SP 500 spectrophotometer was employed for the measurements of absorbance. This was operated by a Doran's Mains unit connected to 220 V./50 cycle a. c. mains, further stabilized by a constant voltage transformer. One centimeter thickness of the solutions was employed by using matched silica cells supplied along with the instrument and distilled water blanks were used. The ultrasensitive phototube was used at wavelengths of 625 mμ or below, and the red sensitive phototube for those above 625 mμ. The phototube circuit was maintained at maximum sensitivity. Under these conditions, the slit width corresponded to very nominal band widths and usually ranged between 0.030 and 0.065 mm.

Colorimetric Measurements.—For these, a Klett Summerson photoelectric colorimeter was employed using the Klett filter No. 54 green (transmission 510~580 mμ). The Klett test tubes in which the solutions were kept for measurements had a uniform diameter of 1 cm.

pH Measurements. — Hydrogen-ion concentration of the solutions was measured with a Leeds and Northrup direct reading pH indicator with a glass calomel electrode system, operated on the aforementioned power mains. The instrument was standardized from time to time with a standard buffer of pH 6.8 supplied along with the same.

Electrical Conductance Measurements.—The measurements of electrical conductance were carried out with a Leeds and Northrup Kohlrausch slidewire with an audio-frequency oscillator in the circuit, operated on the same mains and using a dip type measuring cell having a cell constant 0.580.

Conditions of Study.—All experiments were performed in an air-conditioned room maintained at 30±1°C. The total volume of all the mixtures prepared for the measurements was kept at 50 ml. (variation in the method of continuous variations was done within 25 ml., and the volume then raised to 50 ml. after adding suitable amounts of dextrin and ammonium nitrate, the latter being used for swamping of the system). The individual solutions and mixtures were kept immersed for about an hour, a time which was sufficient for their equilibration and for attaining the temperature of the bath, in a Townson and Mercer's precision thermostat maintaining a temperature of 30±0.01°C. The pH of all the solutions and mixtures was adjusted to 4.5±0.2, by the addition of suitable amounts of sodium hydroxide or perchloric acid. Ionic strength in all the mixtures was also kept constant at 0.15 by the addition of proper amounts of a solution of ammonium nitrate.

Procedure.—The composition of the chelate has been established by employing two different methods viz., (i) the method of continuous variations[10] (using absorbance and electrical conductance measurements) and (ii) the mole ratio method of Yoe and Jones[11] (using absorbance measurements).

Job's method of continuous variations involves the preparation of a series of mixtures with varying mole per cent of the two interactants forming the complex, and the measurement of some physical property of these solutions. A plot of the difference between the observed value and the calculated value of the particular physical property assuming no reaction, should show a maximum or minimum at the mole per cent corresponding to the complex formed.

Despite the various criticisms[12] that have been put against this method, it is still very popular for the study of the composition of complexes in solution, and it is agreed that the results are reliable when absorbance measurements are carried out. In the course of the present studies, electrical conductance was also chosen, besides absorbance, as the index property, and it has been observed that the method yields reliable results not only with absorbance measurements, but with measurements of electrical conductance as well.

In the mole ratio method, a series of solutions is prepared containing a constant amount of the metal ion, but with increasing ratios of reagent to the ion (or vice versa). When the absorbances of these solutions are measured and plotted against the concentration ratios, the plot should be a straight line that rises until the combining ratio of reagent to the metal ion is reached. The curve from this point on should become horizontal unless the reagent itself has some absorbance at the wavelength employed. In such a case the curve should abruptly change slope, but instead of becoming perfectly horizontal, it would have a positive slope, the angle depending upon the degree of absorbance of the reagent solution[13]. No abrupt break in the

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[10] P. Job, *Compt. rend.*, **180**, 928 (1925); *Ann. Chim.*, **(10) 9**, 113 (1928).

[11] J. H. Yoe and A. L. Jones. *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

[12] F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

[13] H. P. Holcomb and J. H. Yoe, *Anal. Chem.*, **32**, 612 (1960).

curve occurs, however, in the case of a complex undergoing appreciable dissociation. In such a case, the continuous curve becomes approximately parallel to the molar ratio axis only when an excess of the variable compound is added. Results obtained by extrapolation of this curve are uncertain but it is found in many cases, that such a curve may be made to break sharply at the correct molar ratio by adjusting the ionic strength to a suitable value by the addition of an indifferent electrolyte14).

Evaluation of the Stability Constant.—The stability constant of the complex has been calculated with the help of absorbance data by two different methods. Anderson and coworkers15) have described a convenient method for the calculation of the stability of colored complexes in solution based on the composition of mixtures having identical color i. e., the same absorbance values. Their method suffers from a limitation that both the interacting solutions forming the complex should be colorless and should not have any absorbance at the $\lambda_{\max}$ of the complex species. This difficulty has been overcome by a modification of this method by Dey and coworkers16) who described a procedure for calculating the stability in the case of complexes where one of the interactants may be colored. The method has thus been found to be more useful and applicable under a wider variety of conditions. The method, in precise, is as follows. Continuous variations method is employed using equimolecular solutions and the total volume is kept constant. The absorbances of the mixtures which are noted at the $\lambda_{\max}$ of the complex are plotted against mole fractions of the metal ion i. e., $[M]/([M]+[Ke])$ ($[M]$ is the concentration of the metal ion and $[Ke]$ that of the chelating agent). The absorbance of the mixtures is due to the color of the chelate and the reagent, since most of the metal ions are colorless at very high dilutions. When the concentration of the metal ions increases progressively (e. g. in the descending portions of the curves), the ligand concentration decreases, and on any point in the descending portions of the curves, a large majority of the reagent may be assumed to be bound up in the complex, and the free chelating agent is negligible to contribute significantly to the total absorbance of the system. The absorbance in these portions is hence, due to the chelate alone, and at the same value of absorbance in a number of such curves, the respective amounts of the complex formed in the individual cases are identical. The concentration of the chelate can be calculated by the following procedure:

In an equilibrium of the type involving a metal ion and a chelating agent in the ratio of 1 : 1,

$$\mathrm{M}+\mathrm{Ke} \rightleftharpoons \mathrm{MKe}$$

the stability constant is given by:

$$K=\frac{x}{(a-x)(b-x)} \tag{1}$$

where x is the concentration of the chelate at equilibrium and a and b respectively are the initial concentrations of the metal ion and the chelating agent. Taking two concentrations of the reactants, i. e., two values of a and b, where absorbance is the same, the value of x will also be the same.

Hence

$$K=\frac{x}{(a_1-x)(b_1-x)}=\frac{x}{(a_2-x)(b_2-x)} \tag{2}$$

or

$$x=\frac{a_1b_1-a_2b_2}{(a_1-b_1)(a_2-b_2)} \tag{3}$$

Thus, it is possible to calculate x, and therefrom the value of K with the help of expression 1.

The value of the stability constant, thus calculated, has also been corroborated by the value obtained by the mole ratio method through a calculation of the degree of dissociation, as suggested by Harvey and Manning17).

Results and Discussion

Rehavior of the Reagent as a Colloidal Electrolyte.—In view of the behavior of a number of dyes as colloidal electrolytes, electrical conductance studies were performed with aqueous solutions of Chrome Azurol S to investigate its colloidal characteristics, if any18). The reagent has been found to behave as a colloidal electrolyte and hence, as emphasized by Dey19) that in the case of colloidal solutions, the characteristics of a true solution are often displayed when extremely dilute solutions are used, very dilute solutions of the order $\approx 10^{-4}$ and 10^{-5} M were employed in the present studies.

Rate of Color Formation and Stability of Color at Room Temperature.—The color formation does not depend upon reaction time and is instantaneous. However, the mixtures were kept for one hour after preparing, to allow for equilibration. A mixture containing 5.0×10^{-5} M thorium chloride and 5.0×10^{-5} Chrome Azurol S at pH 4.5 retained its absorbance value x even after seventy two hours.

TABLE I. INFLUENCE OF TEMPERATURE

Concn. of thorium chloride	5.0×10^{-5} M
Concn. of CAS	5.0×10^{-5} M
pH of the mixture	4.5

Temp., °C	5	10	15	20	30	40	50	60	70	80
Colorimeter reading	268	270	270	270	270	270	280	285	290	295

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14) A. E. Harvey and D. L. Manning., *J. Am. Chem. Soc.*, **72**, 4488 (1950).

15) R. C. Anderson and S. E. Turner, ibid., **70**, 1195 (1948); **71**, 909 (1949); R. T. Foley and R. C. Anderson, ibid., **71**, 912 (1949).

16) A. K. Mukherji and A. K. Dey, *J. Inorg. Nucl. Chem.*, **6**, 314 (1958); *Anal. Chim. Acta*, **18**, 324 (1958); S. K. Banerji and A. K. Dey, Proc. Symp. Chem. Coord. Compds., Agra, 1959, **2**, 198 (1960).

17) A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).

18) S. C. Srivastava, R. L. Seth and A. K. Dey, *J. Colloid Sci.*, **17**, 86 (1962).

19) A. K. Dey, ibid., **3**, 473 (1948).

Influence of Temperature.—The color intensity changes slightly above 40°C, as evident from Table I.

Order of Addition of Reagents.—No appreciable change in observations was found to occur when the order of the addition of reagents was alternated. However, a slightly better sensitivity was obtained, when the reagent solution was added to the metallic ion after the pH and ionic strength of the latter were adjusted to the proper values.

Beer's Law.—A calibration curve was prepared in order to determine whether or not the thorium-Chrome Azurol S complex obeys Beer's law. A series of solutions containing varying amounts of thorium ions and excess reagent were prepared. The color intensity was measured against a reagent blank. A plot of the data showed that the complex concentration is proportional to the absorbance between the concentration limits of 0.23 and 8.35 p. p. m. of thorium, as indicated by the straight lines over this range (Figs. 1 and 2).

Nature of the Complex in Solution. — The method of Vosburgh and coworkers[20] was employed to determine the nature of the complexes formed in solution. Mixtures containing thorium chloride and Chrome Azurol S in different stoichiometric ratios (e. g., 3 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 3, etc.) were prepared and absorbance of each of them was measured at suitable intervals between a range of

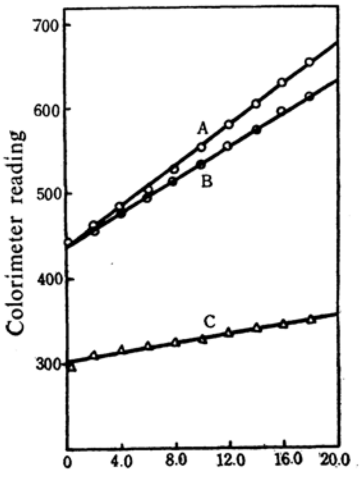

Fig. 1.

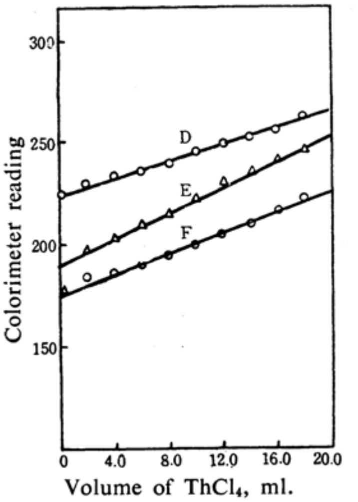

Fig. 2.

Figs. 1 and 2. Adherence to Beer's law.

(Total volume 50 ml.)

20 ml. CAS + x ml. $ThCl_4$ + $(30-x)$ ml. H_2O

Concn. of CAS ($M \times 10^4$): Curve A 2.5, B 2.5, C 1.66, D 1.25, E 1.0 and F 1.0

Concn. of $ThCl_4$ ($M \times 10^4$): Curve A 1.0, B 0.5, C 0.33, D 0.25, E 0.4 and F 0.66

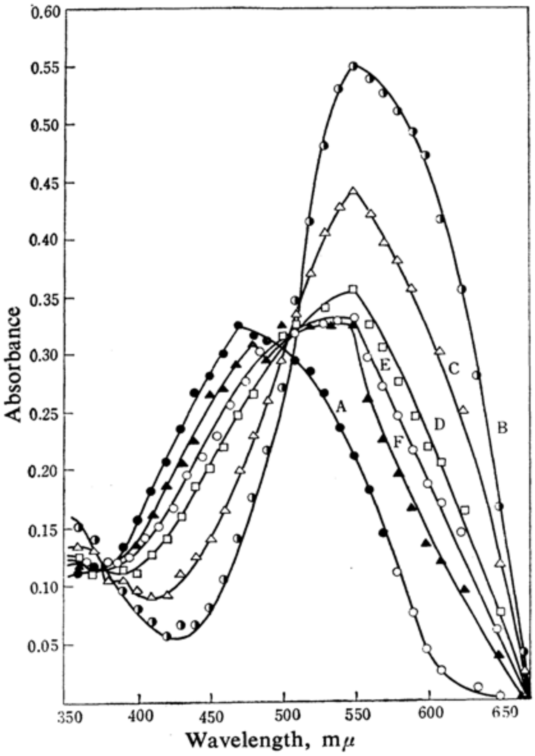

Fig. 3. Absorption spectra studies of mixtures of thorium chloride and Chrome Azurol S, pH 4.5±0.2, μ 0.15 (NH_4NO_3), dextrin 0.1%.

Curve A: Reagent 4.00×10^{-5} M
Curve B: $c = 8.00 \times 10^{-5}$ M, $p = 0.5$
Curve C: $c = 4.00 \times 10^{-5}$ M, $p = 1.0$
Curve D: $c = 2.66 \times 10^{-5}$ M, $p = 1.5$
Curve E: $c = 2.00 \times 10^{-5}$ M, $p = 2.0$
Curve F: $c = 1.33 \times 10^{-5}$ M, $p = 3.0$

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[20] W. C. Vosbugh and coworkers, *J. Am. Chem. Soc.*, 63, 437 (1941); 64, 1630 (1942).

TABLE II

Fig.	Curve	$c\times10^4$ M	p	mμ	Peak occurs at vol. of $ThCl_4$, ml.	Composition of the chelate Th(IV) : CAS
4	A	4.00	1.00	550	12.5	1 : 1
	B	2.66	1.00	550	12.5	1 : 1
	C	2.00	1.00	550	12.5	1 : 1
5	A	4.00	1.00	530	12.5	1 : 1
	B	2.00	1.00	570	12.5	1 : 1
	C	2.66	1.00	530	12.5	1 : 1
6	A	4.00	0.66	530	10.0	1 : 1
	B	2.66	1.50	530	15.0	1 : 1
7	A	4.00	0.66	550	10.0	1 : 1
	B	2.66	1.50	550	15.0	1 : 1

wavelength from 350 to 750 mμ The results plotted graphically in Fig. 3 show that reagent has its maximum absorption at 470 mμ at pH 4.5 (curve A). In curves B, C, D, E and F, the wavelength of maximum absorbance shifts to 550 mμ. In curves E and F, where Chrome Azurol S is present in excess slight peaks near about 485 mμ may be seen to occur. However, in every case, there is a clear indication of the formation of only one complex in solution under the conditions of study having λ_{max} at 550 mμ. (This fact is further confirmed by the results obtained at different wavelengths of study.)

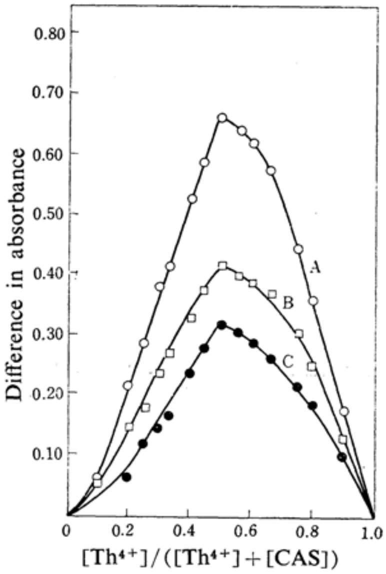


Fig. 4. Determination of the composition from absorption spectra studies of equimolecular solutions at 550 mμ; $p=1$, pH 4.5±0.2, μ 0.15 (NH_4NO_3), dextrin 0.1%.

Curve A: $c=4.00\times10^{-4}$ M
Curve B: $c=2.66\times10^{-4}$ M
Curve C: $c=2.00\times10^{-4}$ M

Stoichiometry of the Components.—The composition was established by the above-mentioned methods using absorbance as well as electrical conductance measurements. Out of a large number of experiments performed some of the typical results have been represented in Figs. 4—13.

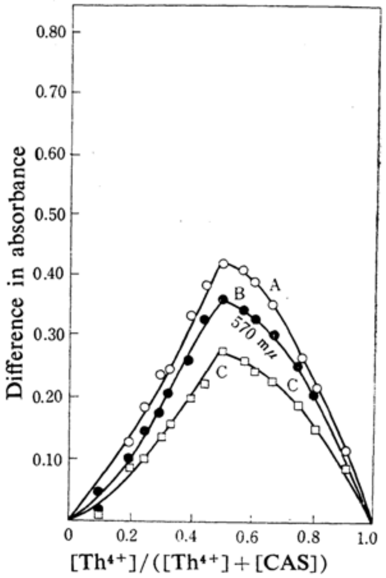


Fig. 5. Determination of the composition from absorption spectra studies of equimolecular solutions at 530 mμ (curve B, 570 mμ); $p=1$. Concentrations, pH and μ same as in Fig. 4.

TABLE III

Fig.	Curve	$c\times10^4$ M	p	Peak occurs at vol. of $ThCl_4$, ml.	Composition of the chelate Th(IV) : CAS
8	A	6.66	1.00	25.0	1 : 1
	B	5.00	1.00	25.0	1 : 1
	C	3.33	1.00	25.0	1 : 1
9	A	3.33	2.00	33.3	1 : 1
	B	3.33	1.50	30.0	1 : 1

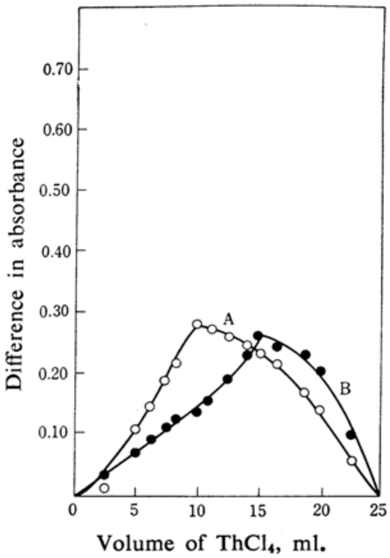


Fig. 6. Determination of the composition from absorption spectra studies of non-equimolecular solutions at 530 mμ; pH 4.5±0.2, μ 0.15 (NH_4NO_3), dextrin 0.1%.

Curve A: $c=4.00\times10^{-4}$ M, $p=0.66$
Curve B: $c=2.66\times10^{-4}$ M, $p=1.50$

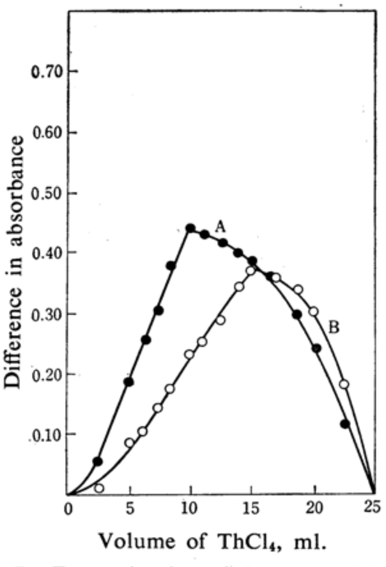


Fig. 7. Determination of the composition from absorption spectra studies of non-equimolecular solutions at 550 mμ. Concentration, pH and μ same as in Fig. 6.

Table II summarizes the results on the composition of the chelate from Figs. 4—7, using the continuous variations method with absorbance measurements. In the legends, c represents the concentration of thorium chloride and p the ratio c'/c, c' being the concentration of Chrome Azurol S.

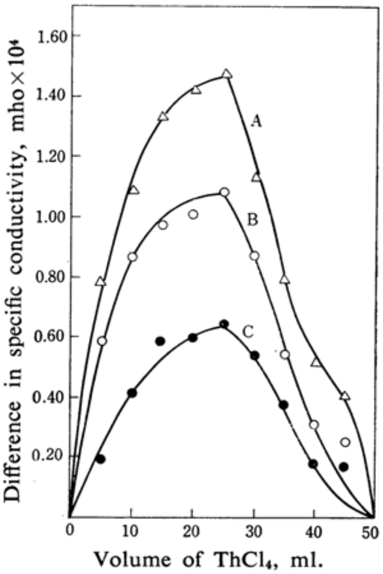


Fig. 8. Determination of the composition from electrical conductance studies of equimolecular solutions ($p=1$).

Curve A: $c=6.66\times10^{-4}$ M
Curve B: $c=5.00\times10^{-4}$ M
Curve C: $c=3.00\times10^{-4}$ M

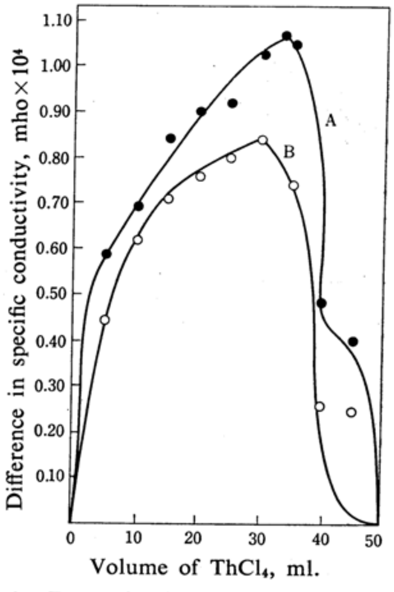


Fig. 9. Determination of the composition from electrical conductance studies of non-equimolecular solutions.

Curve A: $c=3.33\times10^{-4}$ M, $p=2.00$
Curve B: $c=3.33\times10^{-4}$ M, $p=1.50$

The results from the method of continuous variations using electrical conductance measurements (Figs. 8 and 9) are summarized in Table III.

It is perfectly clear from these tables

TABLE IV

Method employed	pH	Ionic strength, μ	Log K	ΔF° at 30°C, kcal.
Method of Dey et al.	4.5 ± 0.2	0.15 (NH_4NO_3)	4.2 ± 0.1	-5.8 ± 0.1
Mole ratio method	4.5 ± 0.2	0.15	4.8 ± 0.1	-6.7 ± 0.1

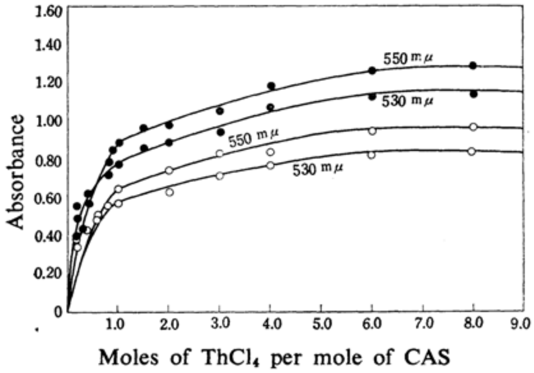


Fig. 10. Determination of the composition from absorbance studies by the mole ratio method; μ not adjusted (Fig. 10), μ 0.15 (NH_4NO_3) (Fig. 11), pH 4.5 ± 0.2, ● concentration of CAS 6.66×10^{-5} M, ○ 5.00×10^{-5} M

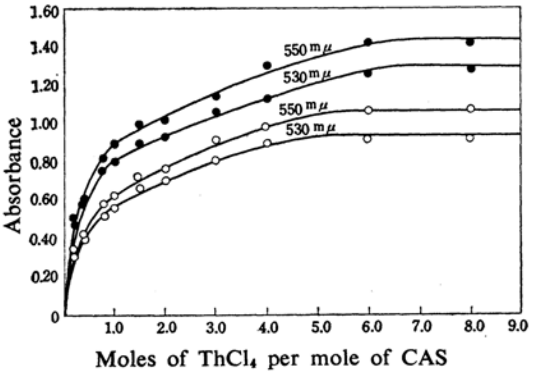


Fig. 11. Determination of the composition from absorbance studies by the mole ratio method; μ not adjusted (Fig. 10). μ 0.15 (NH_4NO_3) (Fig. 11), pH 4.5 ± 0.2, ● concentration of CAS 6.66×10^{-5} M, ○ 5.00×10^{-5} M

that the thorium-Chrome Azurol S chelate consists of one thorium ion to one molecule of reagent, and hence, may be represented as Th (CAS).

Results of the mole ratio method also (Figs. 10 and 11) lend a corroboration for the same composition of chelate.

Calculation of the Stability Constant.—The values of the stability constant (log K), as determined by two different methods outlined earlier, are described in Table IV. The particular values of pH and ionic strength, which were maintained constant, are also mentioned. Also, the free energy change of formation has been calculated with the help of the expression.

$$\Delta F^\circ = -\boldsymbol{R}T\ln K$$

the terms having their usual meaning:

The results obtained by both the methods agree fairly with each other. The values and the methods may, hence, be taken as reliable.

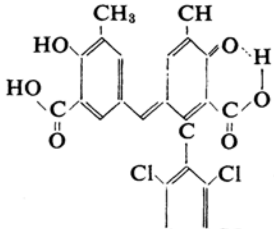
Suggestions on the Structure of the Chelate.—It may be seen from the structure of the reagent Chrome Azurol S, that the trisodium salt is ionizable and in neutral solutions, the compound probably exists as a trivalent anion.

According to the color changes that the compound undergoes with variation in hydrogen-ion concentration of the medium, it may be concluded that it exists in at least three different structural forms. The wavelength of maximum absorbance of the reagent depends upon the pH as follows.

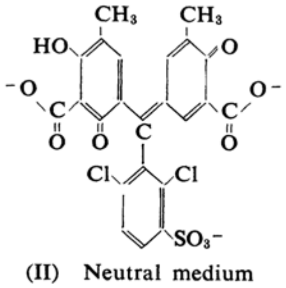
TABLE V

pH	Wavelength of maximum absorbance, λ_{max}, mμ
1.50～5.15	465, 490
6.00～10.15	425
11.65 and above	595

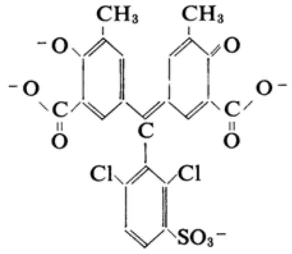
The following structures, therefore, appear to be reasonable for the reagent in the acidic, neutral and alkaline media:



(I) Acidic medium



(II) Neutral medium



(III) Alkaline medium

It is not possible to obtain definite information on the position of the chelate ring in the thorium-Chrome Azurol S chelate from the experimental results described in the present paper. Still it may be evident that there are two alternative positions where chelation might occur. The metal ion may be coordinated either between the quinoid oxygen and the adjacent oxygen of the carboxylic group, or between the phenolic oxygen and the adjacent carboxylic oxygen. It may be noted that the wavelength of maximum absorbance of the chelate is 550 mμ. The λ_{max} of the reagent alone lies at 595 mμ in a strongly alkaline medium, where the structure seems to suggest the removal of the phenolic hydrogen by ionization. In a neutral medium on the other hand, the reagent is observed to have maximum absorption at 425 mμ. Since the wavelength of maximum absorbance of the chelate is more near to that of structure III, rather than to structures II and I it is very likely that the phenolic hydrogen gets replaced during the process of chelation. Hence, it appears reasonable to suggest that the chelation in this case occurs between the phenolic and the carboxylic oxygens and not between the quinoid oxygen and the adjacent carboxylic oxygen.

Effect of Hydrogen-Ion Concentration.—The absorbances of mixtures containing thorium chloride and Chrome Azurol S in the ratio 1 : 1 (concentration of each 8.0×10^{-5} M) at different pH were measured at various wavelengths. Figure 13 shows the results, where it is clearly seen that the wavelength of maximum absorbance of the chelate is 550 mμ from pH 2.50 to 7.25, indicating thereby that the same is stable within this range of pH. The variation with pH in color intensity of the

TABLE VI. TOLERANCE LIMITS FOR DIVERSE IONS

Concn. of thorium chloride	2.0×10^{-5} M
Concn. of CAS	1.0×10^{-4} M
pH of the mixtures	4.5±0.2
Temp.	30°C

Foreign ion	Added as	Concn. of ions p. p. m.	Observed change in absorbance, %	Tolerance limit p. p. m.
Li^+	LiCl	140	−4	
		75	−2	75
Ag^+	$AgNO_3$	432	+6	
		162	+2	Large excess
Pb^{2+}	$Pb(NO_3)_2$	246	+3	
		164	+2	Large excess
Hg^{2+}	$HgCl_2$	62	+5	
		28	+2	28
Cu^{2+}	$CuSO_4$	Interferes at all concentrations		0
Bi^{3+}	$Bi(NO_3)_3$	70	+10	15
		15	+2	
Cd^{2+}	$CdSO_4$	112	+4	
		66	+2	66
AsO_3^{3-}	H_3AsO_3	69	+9	
		18	+2	18
Sb^{3+}	$SbCl_3$	49	+3	
		31	+2	31
Pd^{2+}	$PdCl_2$	Interferes at all concentrations		0
Fe^{2+}	$(NH_4)_2Fe(SO_4)_2$	Interferes at all concentrations		0
Fe^{3+}	$FeCl_3$	Interferes at all concentrations		0
Al^{3+}	$Al(NO_3)_3$	Interferes at all concentrations		
Cr^{3+}	$CrCl_3$	36	+4	
		18	+2	18
La^{3+}	$LaCl_3$	Interferes at all concentrations		0
Mn^{2+}	$MnSO_4$	88	+7	
		28	+2	28
Zn^{2+}	$ZnCl_2$	52	+3	
		39	+2	39

TABLE VI (Continued)

Foreign ion	Added as	Concn. of ions p. p. m.	Observed change in absorbance, %	Tolerence limit p. p. m.
Ni^{2+}	$NiSO_4$	40	+4	
		20	+2	20
Co^{2+}	$Co(NO_3)_2$	34	+3	
		22	+2	22
Ba^{2+}	$BaCl_2$	137	+4	
		68	+2	68
Sr^{2+}	$Sr(NO_3)_2$	90	+3	66
		60	+2	
Ca^{2+}	$CaCl_2$	100	+7	
		30	+2	30
Mg^{2+}	$MgSO_4$	45	+6	
		20	+2	20
Be^{2+}	$BeSO_4$	Interferes at all concentrations		0
Zr^{4+}	$ZrOCl_2$	Interferes at all concentrations		0
Ti^{4+}	$TiCl_4$	Interferes at all concentrations		0
Ce^{3+}	$Ce_2(SO_4)_3$	27	+4	
		15	+2	15
Ce^{4+}	$Ce(SO_4)_2$	24	+5	
		10	+2	10
WO_4^{2-}	Na_2WO_4	56	−4	
		28	−2	28
MoO_4^{2-}	$(NH_4)_2NoO_4$	68	+4	
		40	+2	40
CrO_4^{2-}	K_2CrO_4	93	−6	
		36	−2	36
VO_3^-	NH_4VO_3	60	−3	
		45	−2	45
SeO_3^{2-}	H_2SeO_3	72	+3	
		48	+2	48
TeO_3^{2-}	K_2TeO_3	51	−5	
		22	−2	22
UO_2^{2+}	UO_2SO_4	Interferes at all concentrations		0
Au^{3+}	$AuCl_3$	30	+4	
		15	+2	15
F^-	NaF	Interferes at all concentrations		0
Cl^-	KCl	280	−3	
		180	−2	Large excess
I^-	KI	1280	−4	
		640	−2	Large excess
ClO_3^-	$KClO_3$	664	−3	
		451	−2	Large excess
NO_2^-	$NaNO_2$	460	−3	
		293	−2	Large excess
NO_3^-	$NaNO_3$	310	−5	
		165	−2	Large excess
CNS^-	KCNS	Interferes at all concentrations		0
$B_4O_7^{2-}$	$Na_2B_4O_7$	Interferes at all concentrations		0
CO_3^{2-}	Na_2CO_3	Interferes at all concentrations		0
Oxalate	$K_2C_2O_4$	Interferes at all concentrations		0
Tartrate	K_2 tart.	Interferes at all concentrations		0
Citrate	Na_3cit.	Interferes at all concentrations		0
Acetate	$NaC_2H_3O_2$	280	−6	
		95	−2	95
SO_4^{2-}	K_2SO_4	768	+3	
		576	+2	Large excess
$S_2O_3^{2-}$	$Na_2S_2O_3$	1120	+3	
		784	+2	Large excess
$S_2O_8^{2-}$	$K_2S_2O_8$	960	+8	
		220	+2	Large excess
PO_4^{3-}	NaH_2PO_4	270	−4	
		135	−2	Large excess

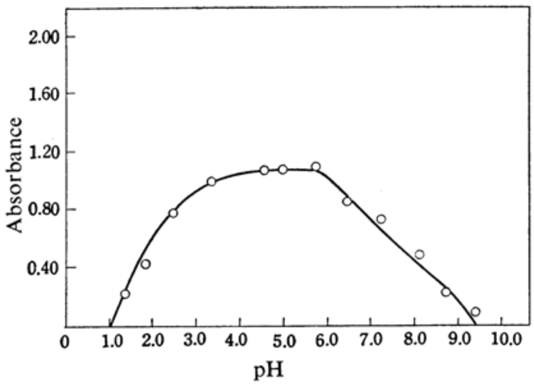


Fig. 12. Variation in color intensity of the chelate with change in pH at 550 mμ.
$c=8.0\times10^{-5}$ M, $p=1.00$

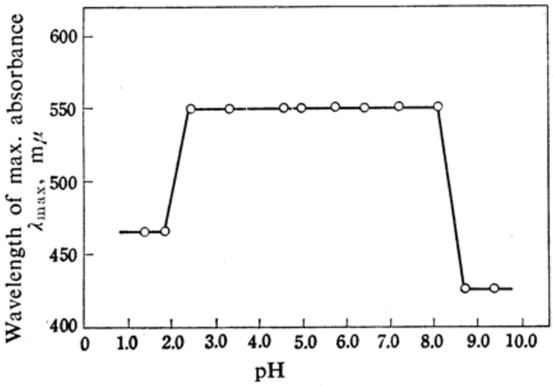


Fig. 13. Variation in the region of maximum absorption of the chelate with change in pH.
$c=8.0\times10^{-5}$ M, $p=1.00$

chelate at its $\lambda_{\max}$ is also represented in Fig. 12.

Sensitivity of the Reaction. — According to Sandell's expression, the sensitivity is 0.0047 γ/cm^2 at 550 mμ. The practical sensitivity, based on an absorbance of 0.010 unit, is 0.047 γ/cm^2.

Effect of Diverse Ions.—The effect of a large number of cations and anions has been studied and the tolerance limits calculated out in each case. For tolerance limit, that concentration of foreign ion has been chosen which affects the absorbance of the system by less than ±2%. It has been found that copper(II), beryllium(II), aluminum(III), iron(II), iron(III), uranium(VI), zirconium(IV), oxalate, borate, citrate, tartrate, carbonate, fluoride and thiocyanate interfere at all concentrations as shown by the results listed in Table VI:

Suggested Procedure for the Colorimetric Determination of Thorium.—For the determination of thorium, using Chrome Azurol S as a reagent, the following procedure may be suggested: The interfering substances should be removed from the sample by the usual methods. The pure solution of thorium ions, thus obtained may directly be treated with a freshly prepared solution of Chrome Azurol S. The reagent should be added in about ten fold molar excess. The temperature should be maintained below 40°C and the pH at 4.5±0.2. The absorbance may be measured with a spectrophotometer and compared with a standard calibration curve to give the amount of thorium.

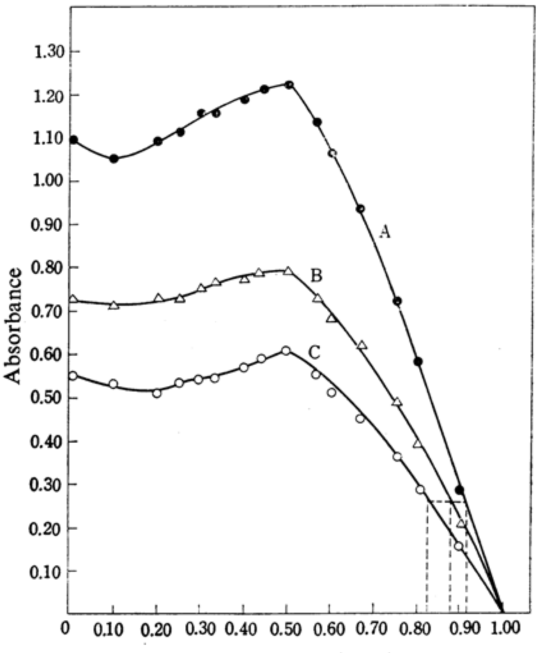


Fig. 14. Determination of the stability constant from absorbance data at 550 mμ. Concentrations, pH and μ same as in Fig. 4.

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