studies in the bromometric determination of vanadium (V) by hydrazine[2]. The present procedure has an advantage that it makes use of As_2O_3, and $KBrO_3$ which are direct primary standards.

Summary

The catalytic action of iodine monochloride on the reduction of vanadium (V) by arsenic (III) has been studied. To a vanadium (V) solution, acidified with hydrochloric acid, a known excess of standard arsenious oxide solutions is added followed by a small volume of dilute iodine monochloride solution. After the reduction of vanadium (V) is complete, the excess arsenious oxide is filtrated against standard bromate using CCl_4. Alternatively the Dead Stop End Point procedure is employed. Arsenious oxide is preferentially oxidised by bromate in presence of vanadium (IV). A method has been suggested for the determination of vanadium (V) As_2O_3 using and $KBrO_3$ as direct primary standards.

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Direct Complexometric Titration of Thorium with Versene using SPADNS

By
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Introduction

Gravimetric methods for the determination of thorium have been long known and widely studied. Of these, methods involving the use of organic precipitants such as 2 : 4-D[5], aryl fatty acids[6] and diphenic acid[1]

are probably the most successful as they possess excellent selectivity for thorium.

The volumetric methods previously available for thorium are indirect, based on the precipitation of thorium with oxalate[11], molybdate[14], oxinate[13] etc. followed by titration of the organic residues or anions. Several other indirect volumetric methods[7, 8] for this element have been recently described by the author. As those indirect methods are time-consuming, rapid volumetric determinations of thorium are desirable.

The direct titration of thorium with ethylenediamine tetraacetic acid using alizarin red S indicator has been recently reported by FRITZ and FORD[9]. In continuation of my search for new and effective reagents for thorium, SPADNS has been found to yield good results for the spectro-photometric determination of microgram amounts of the element[2]. A visual titration of thorium with fluoride based on the disappearance of the blue-violet thorium-SPADNS lake has also been described[3]. As com-plexometric titration (titration with a chelating agent) has become popular in recent years, in the present paper, the use of SPADNS has been made as indicator which permits the rapid and accurate titration of thorium with versene (disodium salt of ethylenediamine tetraacetic acid). The method is based on the fact that thorium forms a blue-violet complex with SPADNS which is less stable than the very strong and colourless thorium-versene complex ($\log K = 23.2$[15]). When a solution of thorium nitrate is titrated with versene in presence of SPADNS as indicator, after a bulk of thorium has reacted with versene, the highly coloured thorium-SPADNS complex is destroyed, making the end point of titration. The method proposed for the complexometric titration of thorium is very rapid and the colour change at the end point is sharp, from blue-violet to scarlet-red. As little as 5 mg. of thorium can be easily titrated by this method. Furthermore, the thorium complex with versene being very stable, moderate quantities of numerous other ions do not interfere, and in certain cases, separations prior to titration need not be -performed. Thorium can be titrated in presence of large amounts of iron by adding ascorbic acid before titration.

Experimental

Reagents and Equipments

Pure SPADNS was prepared as outlined by BANERJEE[3] and its 0.02% solution was made with distilled water.

Standard thorium solutions were prepared by dissolving Merck's pure 552 mg. thorium nitrate tetrahydrate in one litre of distilled water and the thorium content was further estimated by the titrimetric method developed by BANERJEE[3].

Versene, 0.025 M aqueous solution was prepared from 9.3 g. of Merck's pure disodium salt of ethylenediamine tetraacetic acid and dissolving it in one litre.

The solution was standardised against standard calcium carbonate[12] solution using murexide as indicator.

Standard calcium solution was prepared by dissolving 2.4970 g. of B.D.H. reagent grade calcium carbonate, previously dried at 110° C, in dilute hydrochloric acid and diluting it to one litre with distilled water. This solution contained 1.00 mg of calcium per ml. Eastman Kodak, P 6361 murexide was used as indicator for calcium titration. Buffer ($p_H = 3.09$) was prepared from 100 ml (M) sodium acetate solution and 97 ml (M) hydrochloric acid and making the total volume 500 ml with distilled water.

Solutions of all other metals used for interference study, were prepared by dissolving the A.R. quality nitrates, chlorides or sulphates in water, as the case may be, and the metals were estimated by standard methods.

Determination of Thorium

Effect of p_H: In order to find out the range of acid concentration suitable for effective titration, determinations were carried out varying the p_H of the titrating solutions. With SPADNS, satisfactory end points giving quantitative results for thorium, have been obtained in the p_H range 2.5 to 3.5. Results for thorium are not stoichiometric below p_H 2.2 and above p_H 3.5 which will be clear from table 1.

Table 1. *Titration of Thorium at Different* p_H *Values of the Solution.*
Thorium taken = 11.6 mg. Total Volume of the Solution = 50 ml.

p_H	2.0	2.2	2.5	2.8	3.09	3.5	4.0	5.2
0.025 M Versene, ml.	0.98	1.02	1.99	1.98	1.99	2.0	1.80	2.20

So, the p_H of the subsequent titrating solutions has been kept within the desired range by adding acetate-hydrochloric acid buffer in each case.

Effect of temparature: Effect of temperature on the titrating solutions has been studied and in some experiments, the thorium solutions were heated for carrying titrations at different temperatures. It has been observed that heating the thorium solution upto 50° C, there is no alteration of the end point of titration, but above that the thorium-SPADNS lake decomposes and satisfactory end point is not detected.

Concentration of the indicator: 1 ml. of 0.02% SPADNS solution has been found to yield excellent results and accordingly this amount of indicator has been added through the experimental work.

Stoichiometry: In order to ascertain whether the complexometric method for thorium can be made stoichiometric, tests were performed by titrating different aliquots of standard thorium nitrate solution. Results given in table 2 (p. 352) indicate that within ordinary titration error the method is stoichiometric and a 1 : 1 thorium — versene complex is formed.

Table 2. *Titration of Pure Thorium Solutions*

Thorium taken mg.	Theoretical 0.025 M versene, ml.	Actual 0.025 M versene ml.	Diff. ml.
5.80	0.99	0.98	— 0.01
5,80	0.99	0.99	± 0.00
5.80	0.99	0.99	± 0.00
11.60	1.99	2.00	+ 0.01
11.60	1.99	1.99	± 0.00
11.60	1.99	1.98	— 0.01
23.2	3.99	3.99	± 0.00
23.2	3.99	3.98	— 0.01
23.2	3.99	3.98	— 0.01
34.8	5.99	5.98	— 0.01
34.8	5.99	5.99	± 0.00
34,8	5.99	6.01	+ 0.02

Procedure

A solution containing 5 to 34.8 mg. of thorium was taken in an Erlenmeyer-flask. The p_H was adjusted to 3.09 by adding the prepared buffer, 1 ml. of 0.02% indicator and distilled water were added to make the total volume 50 ml. Then the solution was titrated, with swirling, running a standard solution of versene (0.025 M) from a microburette to disappearance of the blue-violet colour. The end point was from blue-violet to scarlet-red. The end point is so sharp that the titration can be done with the natural light and no blank is required comparison. Thorium was calculated as

$$\text{Mg. of thorium} = 232.1 \text{ V.M}$$

where, V = volume of the versenate solution and M = molarity of the same solution.

Titration of Thorium in Presence of Iron

As iron (ic) forms a very strong complex with versene (log K = 25[10]) and iron (ous) forms a comparatively week versene complex (log K = 14.2[10]), it is expected that interference from iron (ic) can be avoided by a preliminary reduction prior to titration. In that case, precaution must be taken to avoid aerial oxidation of Fe (ous) to Fe (ic) during the experiment. Moreover it has been observed that when the ratio of Th : Fe (ous) exceeds 1 : 10, Fe (ous) interferes in the titration. During the present investigation, thorium has been directly titrated in presence of iron (ous & ic) by adding ascorbic acid before titration. Therefore, the addition of ascorbic acid permits the quantitative determination of thorium in presence of iron (ous & ic). Some results of titration of mixtures containing thorium and iron are given in table 3.

Table 3. *Titration of Thorium in Presence of Iron.* Initial Volume = 50 ml.

Expt. no.	Metals taken mg.	Ascorbic acid added, g.	Thorium found mg.	Diff. mg.
1.	Th 11.6 Fe^{II} 55.0		11.50	— 0.10
2.	Th 11.6 Fe^{II} 110.0		11.35	— 0.25
3.	Th 11.6 Fe^{II} 165.0	1.0	11.58	— 0.02
4.	Th 11.6 Fe^{III} 10.0	0.5	11.60	± 0.00
5.	Th 11.6 Fe^{III} 25.0	1.0	11.59	— 0.01
6.	Th 11.6 Fe^{III} 75.0	1.0	11.58	— 0.02

Study of Interferences

Interfering and noninterfering ions are listed in table 4. No interference has been detected with chloride, nitrate, acetate etc. As might be expected, such anions as fluoride, sulphate, molybdate, phosphate, tartrate, citrate, alginate and tungstate interfere seriously. Most of the cations, when present in 10 times to the thorium concentration do not interfere in the titration which will be revealed from table 4. As zirconium

Table 4. *Effect of other Ions on Titration of 11.60 mg. of Thorium*

Ion added*	Substance	Theoretical versene ml.	Actual versene ml.	Ion added*	Substance	Theoretical versene ml.	Actual versene ml.
Li$^+$	LiCl	1.99	1.98	Al^{+++}	Al$_2$(SO$_4$)$_3$	1.99	1.98
Na$^+$	NaNO$_3$	1.99	1.99	La^{+++}	La(NO$_3$)$_3$	1.99	2.01
K$^+$	KNO$_3$	1.99	1.98	Ce^{+++}	Ce(NO$_3$)$_3$	1.99	2.02
NH$_4^+$	NH$_4$NO$_3$	1.99	1.99	Mo^{+++}	MoCl$_3$	1.99	Interferes
Ag$^+$	AgNO$_3$	1.99	Interferes	Cr^{+++}	CrCl$_3$	1.99	2.2
Hg^{++}	Hg(NO$_3$)$_2$	1.99	2.00	Sb^{+++}	SbCl$_3$	1.99	Interferes
Pb^{++}	Pb(NO$_3$)$_2$	1.99	Interferes	Bi^{+++}	BiONO$_3$	1.99	Interferes
Cu^{++}	CuSO$_4$	1.99	Interferes	Ce^{++++}	Ce(NO$_3$)$_4$	1.99	Interferes
Cd^{++}	CdCl$_2$	1.99	1.98	Ti^{++++}	TiCl$_4$	1.99	Interferes
Sn^{++}	SnCl$_2$	1.99	Interferes	Sn^{++++}	SnCl$_4$	1.99	Interferes
Ca^{++}	CaCl$_2$	1.99	1.98	F$^-$	NaF	1.99	Interferes
Sr^{++}	Sr(NO$_3$)$_2$	1.99	1.98	Ac$^-$	Na-acetate	1.99	1.97
Ba^{++}	BaCl$_2$	1.99	1.99	VO$_3^-$	NaVO$_3$	1.99	1.95
Mg^{++}	MgCl$_2$	1.99	1.98	MoO$_4^{--}$	Na$_2$MoO$_4$	1.99	Interferes
Ni^{++}	NiSO$_4$	1.99	Interferes	WO$_4^{---}$	Na$_3$WO$_4$	1.99	Interferes
Co^{++}	CoSO$_4$	1.99	1.98	Citrate	Na-citrate	1.99	Interferes
UO$_2^{++}$	UO$_2$(NO$_3$)$_2$	1.99	Interferes	Oxalate	Na-oxalate	1.99	Interferes
V^{++}	VCl$_2$	1.99	Interferes	Tartarate	Na-tartarate	1.99	Interferes

* approximately 10 times to the concentration of thorium.

forms a strong lake with SPADNS, and its interference is quantitative, the work on the complexometric titration of zirconium has already been taken separately[4].

Discussion

Thoug the complexometric titration with EDTA or Versene has become much popular now a days, the lack of good indicators could not extend the usefulness of the reagent for the direct titration of thorium. Now, however, new indicator SPADNS has been found which permits the rapid and accurate titration of microgram amounts of thorium with versene. The blue-violet colour due to the thorium-SPADNS lake turns into scarlet-red at the end point which can be easily detected visually.

Summary

The existing volumetric methods for the determination of thorium are indirect and unsatisfactory. A direct titrimetric method for the estimation of thorium has been developed which involves the adjustment of p_H, addition of 1 ml. of 0.02% SPADNS indicator, dilution to volume and titration with versene. It is based on the fact that thorium forms a coloured complex with SPADNS and after the bulk of thorium has reacted with versene, the highly coloured thorium- indicator complex is destroyed, marking the end point. Quantity of thorium as small as 5 mg. can be titrated accurately when present in a volume of 50 ml. Determination of thorium can also be made in presence of large amount of iron by adding ascorbic acid prior to the titration. Interferences of various ions have also been studied. The method proposed for thorium is selective and should be of considerable use in many cases.

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