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COMMISSION OF THE EUROPEAN COMMUNITIES

**THE PRECISE COMPLEXIMETRIC DETERMINATION
OF THORIUM**

by

A. BRÜCK and K.F. LAUER

1971



**Joint Nuclear Research Centre
Geel Establishment - Belgium**

Central Bureau for Nuclear Measurements - CBNM

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The precise compleximetric determination of thorium *)

1. Introduction

As the thorium ion exists only in the valency state + IV in aqueous solution, no reaction involving oxydation or reduction is known. Therefore thorium can only be determined by gravimetric, volumetric or spectrophotometric methods. The usual photometric methods are generally applied to small quantities of thorium and are not very precise unless a differential spectrophotometric method is used (1). If a pure solution of thorium has to be analyzed with great precision only the gravimetric or compleximetric method can be applied. Of these two last methods only the compleximetric one can be used if the concentration of the thorium in the solution is low. The determination of thorium with chelating agents such as the disodium (ethylenedinitrilo)-tetraacetate dihydrate (EDTA) has been described by several authors. Thorium forms a 1:1 complex with EDTA and the value of the log of the stability constant at 20° at an ionic strength of 0.1 as determined by polarography is 23.2 ± 0.1 . (2). Cabell described the formation of the thorium - EDTA complex in 1952 (3). Since then numerous indicators have been proposed for the direct or indirect determination of thorium. Fritz and Ford (4) determined thorium with Red Alizarin S and several other indicators have been described such as Arsenazo, pyrocatechol violet, SPADNS, thorin and Xylenol orange (5) (6) (12). As the determination is carried out in an acidic medium (pH 2,3 - 3.4) few metals form complexes with EDTA which renders the method rather selective.

To improve specificity the use of T.C.A. (Dithio-carbaminoacetic acid) as a masking agent in the titration

*) Manuscript received on July 22, 1971

of thorium has been investigated (7). This material has been shown to mask In (III), Bi (III), Cr (III), Ni (II), Cu (II), Pb (II) and Al (III). Fe (III), Sc (III), Zr (IV) and Ti (IV) are not masked and interfere quantitatively.

Of all the described indicators the best endpoint indication is obtained with xylenol orange prepared by Pribl et al. (8).

In an acidic medium this indicator has remarkable properties. Compleximetric determinations of Bi (III), Th (IV), Sc (III), Pb (II), Zn (II) and Cd (II) has been described (8). In the case of the thorium titration, even in solutions which are not buffered, the endpoint indication from red to lemon yellow, is surely one of the best ever seen in compleximetric titrations. The composition and the stability of the thorium-xylenol orange complex have been studied by Budesinsky (9). We have already described the technique of the titration in the case of the compleximetric determination of uranium (11). The endpoint is detected visually for large quantities of thorium, whereas for small quantities, down to 5 mg metal per determination, we have applied the photometric endpoint detection.

2. Determination of thorium

2.1. Experimental: Instruments, equipment and reagents

For measurements and adjustment of the pH a Knick pH meter (type 350) fitted with a combined glass-calomel electrode was used. The addition of the EDTA solution was done partially with a weight burette and partially with the calibrated Metrohm burette E374 of 1 ml (± 0.0003 ml) capacity. The extinction measurements were performed with the Cary recording spectrophotometer, model 11-50, whilst the titration cell (10) had a light path of 5 cm. All the reagents were of reagent grade

quality, the water was twice-distilled from quartz and the thorium metal provided by Metal Hydrides Inc. had been prepared by the iodide process.

2.1.1. Standard EDTA solution

The preparation and the standardization of the EDTA solutions have been described in detail (11). The molarity of the EDTA solutions varried from 0.05 M for the greatest quantities of thorium to 0.0004 M for the quantities of 0.1 mg thorium per determination.

2.1.2. Standard thorium solution

The analysis report of the thorium metal provided by Metal Hydrides Inc. indicated the following impurities.

Element	Typical, ppm	Limiting, ppm
O	32	50
N	20	20
H	8	10
C	20	40
Al	3	20
Fe	23	30
Cu	12	20
Mg, Ca, Si, Mu, Cr, Ni, Ti, B	2	3
other metals	not spectrogra- phically de- tected in typi- cal runs	

Table 1. Impurities indicated by the supplier of the thorium metal.

A standard thorium solution was prepared by dissolving under reflux in quartz 10 g of the metal in tridistilled nitric acid,

to which 3 drops of a very diluted hydrofluoric acid had been added. After dissolution the excess of acid was removed by heating gently to near dryness, the thorium salt was taken up in water and the solution made up to a known weight. The acidity of the solution was about 0.1 N. More dilute solutions were made by gravimetric dilution.

2.1.3. Indicator

For the visual titrations the indicator was prepared by mixing 1 g xylenol orange with 99 g of suprapur KCl. For the titrations with a spectrophotometric endpoint detection a 0.1 % aqueous solution of xylenol orange was used.

2.2. Titration of the thorium

2.2.1. Procedure using a visual endpoint detection technique

20 g of a thorium solution containing about 250 to 1 mg to 1 mg thorium are introduced with a weight burette into a 250 ml beaker. The EDTA solution is added gravimetrically in such a quantity that the endpoint is nearly reached. The solution is diluted with water to a volume of approximately 150 ml. The pH of the solution is adjusted with a diluted ammonia solution to a value of 3.0 ± 0.1 . The indicator is added and the titration is completed with the same EDTA solution using the calibrated microburette of 1 ml. The quantity of titrant added volumetrically is less than 0.1 ml. The endpoint is easily detected by the sharp change of the indicator from red to lemon yellow. The results are reported in table 2. A look at this table shows that S (coefficient of variation) increases rapidly at quantities below 5 mg. The systematic error appeared also to increase with smaller quantities. Therefore we have adopted in this range another procedure, employing a photometric endpoint detection technique.

Table 2. Results of the compleximetric determinations using a visual and a photometric endpoint detection technique.

Th given (mg)	Th found (mg)	Δ (found-given) (mg)	σ %	n	endpoint
267.000	267.050	0.05	0.045	7	visual
155.000	155.028	0.028	0.035	12	"
51.000	50.990	0.01	0.024	12	"
25.000	26.000	0.00	0.012	10	"
10.000	9.998	0.002	0.034	11	"
5.000	4.996	0.004	0.041	11	"
5.000	4.996	0.004	0.11	11	photomet.
1.000	0.990	0.010	0.34	10	visual
1.000	0.998	0.002	0.31	11	photomet.
0.500	0.4990	0.001	0.37	12	"
0.250	0.2472	0.0028	0.30	12	"
0.100	0.0965	0.0035	0.28	9	"

A glance at table 2 shows that there are no problems to reach a precision and an accuracy better than 0.1 % for quantities greater than 5 mg thorium per determination. Quantities from 5 mg down to 0.5 mg per determination should be determined by photometric endpoint detection giving a good precision and accuracy. The method shows a very slight and constant negative systematic error of about 3 μ g thorium. For the determinations of quantities of Th above 5 mg Th per determination this systematic error is negligible and disappears within the limits of the reproducibility of the method. For quantities below 5 mg a correction for this systematic deviation will have to be applied to the factor of the strength of the titrant. It is evident that the above method allows the titration of smaller quantities of thorium with reproducibilities of several per cent (e.g. 10 ± 1 μ g Th).

2.2.2. Procedure using a photometric endpoint detection technique

We shall give a detail example for a quantity of 0.5 mg thorium per determination. 10 g of a thorium solution containing 0,2644 mg Th/g are introduced with a weight burette into a beaker. 50 ml of water are added and the pH is adjusted in such a way that if the solution is transferred to a 100 ml volumetric flask and 0.5 ml of the indicator solution is added, the pH of the solution will be 3.0 ± 0.1 . The solution is homogenized and after a short time the volumetric flask is weighed 20 ml of this solution are introduced in the cylindrical cell provided with the cell attachment for photometric titrations (10). One introduces approximatively 96 % of the EDTA solution (0.0005 M) gravimetrically and the following titration is done volumetrically by adding portions of 0.02 ml of the same titrant with the microburette of 1 ml capacity. After each addition the optical density is measured at a wavelength of 570 nm. Fig. 1 shows such a titration curve in the vicinity of the endpoint. The same technique is used for quantities of 5 mg and 1 mg thorium per determination, whilst for 0,25 mg and 0,1 mg thorium the addition of the titrant is done volumetrically. The results obtained are shown in table 2.

3. Results and discussion

The results of the thorium titration by both procedures are shown in table 2. n denotes the number of determinations, S % the coefficient of variation and Δ the deviation in mg from the theoretical value.

4. Use of thorium metal as a standard

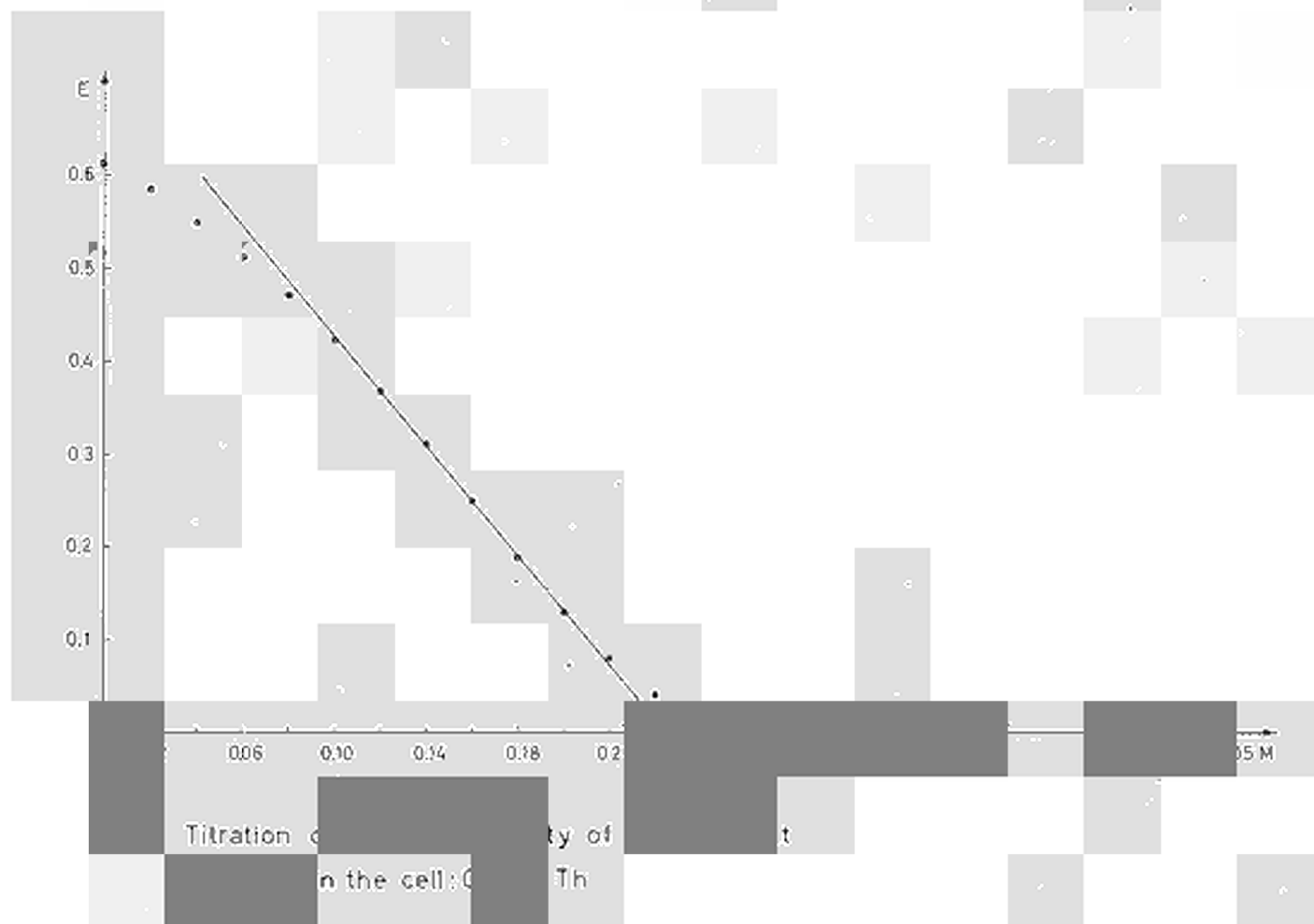
From the above measurements it can be concluded that the metal that is at our disposal would probably be suitable as starting material for the preparation of a thorium reference sample. The values found agree very well ($< 0.05\%$) with the nominal weight of thorium taken for the analysis. The homogeneity should be checked on greater batches of such a metal. The metal has a bright appearance and does not seem to have tarnished since we have obtained it (2 years). The Central Bureau for Nuclear Measurements is preparing a programme for the preparation and definition of a chemical thorium standard.

5. Acknowledgment

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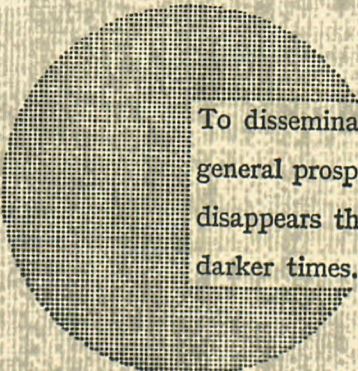
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Alfred Nobel

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