

Volumetric and Spectrophotometric Microdetermination of Cerium(III), Thorium(IV) and Uranium(VI) in some Chelates of 3-Acetyl- and 3-Cyano-1,5-diarylformazans

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The title chelates are analysed through their oxidative destruction either by the Kjeldahl method or more rapidly by the oxygen flask method, followed by the microdetermination of the cations by suitable spectrophotometric methods besides a parallel conventional volumetric confirmation methods. Ce^{III} is determined as the yellow formaldoxime complex measured at 400 nm in the range 0-20 ppm. Volumetrically, it is oxidised to Ce^{IV} , then reacted with $FeSO_4$, and the excess of which is back-titrated with $KMnO_4$. Th^{IV} is determined as the arsenazo III complex measured at 660 nm in the range 1-25 $\mu g/25$ ml. A parallel complexometric titration using xylenol orange as indicator is performed. U^{VI} is determined as its PAN complex at 555 nm in the range 1-20 ppm. A complexometric titration at pH 4.4 in isopropanol containing medium using PAN also as indicator, is parallely done. The results are within the acceptable limits.

Elemental analyses in the case of arsono derivatives are not satisfactory. Analysis of the metal content using thermogravimetric method of analysis is not convenient in other cases where the functional group does not involve arsono group¹. This led to search for new method to analyse such complexes using the oxygen flask.

The present investigation deals with the evaluation of new methods for the determination of metal content in organic-metal chelates. The compounds used are the Ce^{III} , Th^{IV} and UO_2^{VI} complexes of 3-acetyl or 3-cyano-1,5-diarylformazan. The determination of the concentration of the chelated metal ion is conducted through mineralisation by wet digestion in Kjeldahl flask, or by the oxygen flask where possible, followed by a suitable spectrophotometric method and confirmed parallely by a volumetric one.

Results and Discussion

The advantage of the method reported is mineralisation of organometallic compounds. The organic moiety is completely decomposed during combustion and does not interfere. The oxygen flask

method presents an efficient and rapid alternative that can be easily achieved along with Kjeldahl method. For convenience, every cation is discussed separately.

Ce^{III} : The use of 10 ml of 2 M HNO_3 , 1:1 H_2SO_4 or even their concentrated solutions as absorbent during decomposition in conjunction with Pt-gauze or silica spiral as sample holder, resulted in very low recoveries. Since CeO_2 is a rather inert substance², the flux was essential. In this method, after combustion, the content is boiled for 40 min to assure the complete dissolution of any insoluble salts. The exculsion of this digestion step resulted in very low recoveries. The problem in the determination of organocerium(III) compounds is that their decomposition, regardless the method used, results in the oxidation of varying amounts to the Ce^{IV} state, i.e. both Ce^{III} and the Ce^{IV} ions are present. This was proved through the scanning of the absorption spectra of the decomposition mixture in 1 N H_2SO_4 medium in the uv region³, where the Ce^{III} showed a sharp maximum at 193 nm and the Ce^{IV} a broad one at 290 nm. So the aim of the work was the reduction of Ce^{IV} to the Ce^{III}

TABLE 1 – VOLUMETRIC AND SPECTROPHOTOMETRIC
 MICRODETERMINATION OF Ce^{III}, Th^{IV} AND U^{VI} COMPOUNDS
 % Ce

Compd. Formula	Volumetric		Spectro- photometric
	Cal	Found*	Found*
Ce(III) oxalate	38.68	38.81(0.209)	38.85(0.189)
Ce(C ₂ O ₄) ₃ · 10H ₂ O			
Ce - Ia (1 : 1)	25.56	25.46(0.180)	25.33(0.088)
Ce{(C ₁₅ H ₁₃ N ₄ O · 4H ₂ O)Cl			
Ce - Ia (1 : 2)	18.89	18.40(0.083)	18.39(0.097)
Ce{(C ₁₅ H ₁₃ N ₄ O) ₂ · 2H ₂ O}Cl			
Ce - IIa (1 : 1)	27.97	27.42(0.159)	27.20(0.235)
Ce{C ₁₄ H ₁₀ N ₅ · 2H ₂ O}2OH			
Ce - IIb (1 : 1)	26.43	25.76(0.109)	26.11(0.154)
Ce{C ₁₅ H ₉ N ₅ O ₂ · 2H ₂ O · C ₂ H ₅ OH}OH			
Ce - IIc (1 : 2)	15.21	15.02(0.128)	15.01(0.080)
Ce{(C ₁₄ H ₁₀ N ₅ O ₃ As ₂ · 2H ₂ O)OH			
Ce - Id (1 : 1)	20.33	20.49(0.216)	20.44(0.178)
Ce{(C ₁₅ H ₁₃ N ₄ O ₇ As ₂ · 2H ₂ O)OH			
Ce - IId (1 : 2)	12.38	12.46(0.090)	12.45(0.093)
Ce{(C ₁₄ H ₁₁ N ₅ O ₆ As ₂) ₂ }OH			
Thorium oxalate	44.95	44.98(0.187)	45.10(0.183)
Th(C ₂ O ₄) ₂ · 6H ₂ O			
Th-acetylacetonate	36.92	36.76(0.207)	36.80(0.132)
Th(C ₅ H ₇ O ₂) ₄			
Th - Ia (1 : 1)	39.06	38.94(0.162)	38.98(0.118)
Th{(C ₁₅ H ₁₃ N ₄ O · 3OH · C ₂ H ₅ OH)}			
Th - Ia (1 : 2)	26.13	26.20(0.126)	26.22(0.125)
Th{(C ₁₅ H ₁₃ N ₄ O) ₂ · 2C ₂ H ₅ OH}2OH			
Th - Ib (1 : 1)	32.31	32.20(0.136)	32.18(0.125)
Th{C ₁₆ H ₁₂ N ₄ O ₃ · 3H ₂ O}2NO ₃			
Th - Id (1 : 1)	29.78	29.69(0.081)	29.71(0.116)
Th{C ₁₄ H ₁₀ N ₅ O ₆ As ₂ · 2H ₂ O}OH			
Th - Id (1 : 2)	18.47	18.39(0.080)	18.42(0.078)
Th{(C ₁₅ H ₁₄ N ₄ O ₇ As ₂) ₂ }			
Th - IIc (1 : 2)	22.97	23.01(0.133)	22.98(0.106)
Th{(C ₁₅ H ₁₀ N ₅ O ₃ As) ₂ · 2H ₂ O}			
Uranyl acetate	56.14	56.32(0.197)	56.23(0.173)
UO ₂ (CH ₃ COO) ₂ · 2H ₂ O			
UO ₂ Ia (1 : 1)	39.27	39.41(0.145)	39.36(0.124)
UO ₂ {C ₁₅ H ₁₃ N ₄ O · 3H ₂ O}OH			
UO ₂ - Ia (1 : 1)	28.46	28.34(0.108)	28.38(0.085)
UO ₂ {(C ₁₅ H ₁₃ N ₄ O) ₂ · 2H ₂ O}			
UO ₂ - Ib (1 : 1)	38.69	38.54(0.166)	38.61(0.131)
UO ₂ {C ₆ H ₁₂ N ₄ O ₃ · 3H ₂ O}			
UO ₂ - Ib (1 : 2)	25.75	25.59(0.101)	25.67(0.084)
UO ₂ {C ₁₆ H ₁₃ N ₄ O ₃ } ₂ · 2H ₂ O}			
UO ₂ - Id (1 : 1)	29.09	29.22(0.139)	29.19(0.116)
UO ₂ {C ₁₅ H ₁₄ N ₄ O ₇ As ₂ · 2H ₂ O}			
UO ₂ - Id (1 : 2)	18.36	18.27(0.082)	18.29(0.069)
UO ₂ {(C ₁₅ H ₁₄ N ₄ O ₇ As ₂) ₂ }			

*Average of 4 determinations; figure in parenthesis indicates standard deviation.

the Ce^{III} form is oxidised to Ce^{IV} as applied in the volumetric method. This method⁴ is successfully scaled down to suit the micro-scale and clear end-points are detectable in all cases. In case of samples decomposed by HCl, the addition of both ammonium persulphate and sodium bismuthate does not result in the oxidation of Ce^{III} to Ce^{IV}, instead a white heavy precipitate of NH₄Cl appears. The addition of concentrated H₂SO₄ (1 ml) and boiling the solution to expell HCl before the addition of the oxidants, give more accurate results (Table 1).

Th^{IV} : The decomposition procedure determines to a great extent, the rapidity, easiness and accuracy of the determination. Applying the only available procedure⁵, inconsistently low recoveries were obtained in all cases, even with the use of more concentrated acid solutions. Moreover, after repeated combustions, Pt-gauze was damaged and a white precipitate was observed in the absorption solution. This is in accordance with the difficult solubility of Th compounds⁶ especially ThO₂ in concentrated acids. To solve the difficulty, the silica spiral as sample holder was used. Similar low recoveries were obtained besides the occurrence of incomplete combustion in some cases. We tried to combust an inorganic salt, namely thorium nitrate in the oxygen flask following the reported conditions⁵, but no quantitative recoveries were obtained. Thus wet digestion in Kjeldahl flasks is recommended as the possible decomposition procedure. The use of concentrated HNO₃ as the digestion medium is advantageous for its ease of complete removal through repeated evaporation. The residue with water gives a solution where pH is suitable for the spectrophotometric determination using 0.1% aqueous arsenazo III reagent. A lower range of determination (0.08–1 ppm) was possible. The complexometric method, though very simple, covers the range 1–3 mg Th (Table 1).

U^{VI} : The method available for determination of organo-uranium depends on ignition⁷ to U₃O₈ or through digestion with sulphuric acid. A trial to use a Pt-gauze sample holder and use of 2 N HNO₃ (5 ml) as absorbent⁸ was unsuccessful with only a 65–75% recovery. It was reported that ignition of organic uranium compounds in Vycor, quartz or platinum crucibles could result in small amounts of U adhering firmly to the crucible surface which

and the removal of excess reductant. Alternatively,

could resist recovery even by fusion methods⁹. Addition of bisulphate before ignition can prevent this loss. For this sake, a silica spiral as sample holder was used with 2 M HNO₃ solution (10 ml) as absorbent. Six uranium chelates in addition to uranyl acetate were decomposed quantitatively by the present procedure (Table 1). There was no need for addition of a flux. In the complexometric method of estimation, the colour change of the PAN indicator from red to yellow was quite sharp. The use of PAN reagent, also in the spectrophotometric procedure, enables the determination of U^{VI} in the range 1–20 ppm. Both the methods showed high selectivity.

In general, in the analysis of As containing chelates, the end-point detection is very difficult by complexometric method but not by spectrophotometric method.

Some known salts and complex of Ce, Th and U were analysed as a sort of calibration of the methods used. Both the spectrophotometric and the volumetric methods gave satisfactory results with the chelates of the three cations. The average standard deviations for the volumetric and spectrophotometric methods, are 0.147 and 0.139 for Ce^{III}, 0.139 and 0.123 for Th^{IV} and 0.134 and 0.112 for UO₂^{II} respectively.

Experimental

Standard stock solutions (1000 ppm) of Ce^{III}, Th^{IV} and U^{VI} were prepared by the dissolution of their hexahydrated nitrates in water. EDTA solutions (0.01 and 0.025 M) were standardised⁴. Aresnazo III and xylenol orange (0.1% aqueous) and PAN (0.1% ethanolic) solutions were used as indicators. A 10% ethanolic solution of triethanolamine was prepared.

Solutions (0.005 N) of each of FeSO₄ and KMnO₄ were prepared and standardised. Acetate buffer (pH 5) was prepared by mixing 0.1 M acetic acid (100 ml) with 0.1 M sodium acetate (200 ml). Formaldoxime reagent (1 M) was prepared by mixing formaline solution (38%; 7.9 g) with hydroxylamine hydrochloride, (A.R.; 7 g) and diluted to 100 ml with water; this solution was made 1 M with respect to HCl.

The solid complexes were prepared as reported earlier¹.

A Shimadzu UV 240 spectrophotometer provided with 1 cm quartz cell was used.

(A) *The decomposition procedure : Decomposition in the Kjeldahl flask* : Th^{IV} and U^{VI} samples in the range 5–15 mg, were digested in 50 ml-flask using concentrated HCl (5 ml). The time of boiling, in general was 2–3 h.

Decomposition by the oxygen flask : Ce^{III} chelates sample (5–7 mg in the case of applying the spectrophotometric method or 10–15 mg in case of the volumetric method) was put into the conventional¹⁰ ashless filter paper corner. To it finely powdered Na₂CO₃ (~20 mg) was added and thoroughly mixed with the sample using a Pt-wire, then the paper was closed as usual¹⁰ and fixed into the Pt-gauze sample holder. A 500 ml oxygen flask was charged with 10 ml of 1 : 1 H₂SO₄ or 6 M HCl or concentrated HNO₃ solution (25%) as absorbent, and flushed with oxygen for 1 min. The contents after combustion of the sample were transferred quantitatively with water to a 50 ml-volumetric flask.

The procedure for uranium chelates was similar to the cerium compounds, except for the use of silica spiral as the sample holder instead of the Pt-gauze and the exclusion of Na₂CO₃ flux addition to the sample. Also 2 M HNO₃ (10 ml) was used as absorbent, the boiling step after combustion was extended till nearly to dryness with repeated rinsing with water to assure the complete removal of HNO₃.

(B) *The methods of estimation* :

Volumetric methods : For estimating Ce^{III} ion, a solution containing 1 mg Ce^{III} and concentrated H₂SO₄ (0.2–0.7 ml) mixed with ammonium persulphate (0.1 g) and sodium bismuthate (0.1 g), was boiled for 5 min, filtered through a sintered disc using 2% H₂SO₄ solution for washing. Excess 0.005 N ferrous sulphate solution was then added and titrated with 0.005 N KMnO₄ to the first appearance of the pink colour⁴.

In case of samples decomposed by HCl, whether by wet digestion or in the oxygen flask, concentrated H₂SO₄ (1 ml) was added and the mixture boiled

for 1 min to expell the HCl before the addition of persulphate and bismuthate.

For estimating Th^{IV} ion, dilute ammonia was added to a solution containing 1–3 mg Th until pH 5 where the precipitate dissolved with difficulty. Then the acetate buffer (pH 5; 10 ml), pyridine (1 drop) and xylenol orange indicator (6 drops) were added. The solution was then titrated with 0.025 M EDTA untill the colour changed from red to yellow¹¹.

For estimating U^{VI} ion a solution containing ~10 mg U was adjusted to pH 2–3, then to 4.4 by hexamethylenetetramine. Then isopropyl alcohol (10 ml) was added and the mixture was heated to 80–90° followed by addition of PAN indicator (1–2 drops) and titration with 0.025 M EDTA solution from red to yellow¹².

Spectrophotometric methods :

For estimating Ce^{III} ion, an aliquot (5–10 ml, according to the expected concentration) was mixed with hydroxylamine hydrochloride (50–100 mg) and shaken well for dissolution. The mixture was boiled on a hot-plate for 5 min, cooled and transferred quantitatively to a 25 ml-volumetric flask. To it was added formaldoxime reagent (2.5 ml) followed by the dropwise addition of NaOH solution (~5 M) till the appearance of yellow colour of the reagent proving complete neutralisation. Then 1 M NaOH solution (2 ml) was added to ensure alkaline medium, made up to the mark with water and mixed thoroughly, and the absorbance was measured at 400 nm after 10 min¹³.

For estimating Th^{IV} ion, an aliquot containing 1–25 µg Th was mixed with concentrated HCl (6 ml) and 0.1% aqueous solution of Aresenazo III, then made upto 25 ml with water. Its absorbance was measured at 660 nm¹⁴.

For estimating U^{VI} ion, PAN reagent (1 ml) was mixed with aqueous solution containing 1–20

µg U and the volume made upto 10 ml with ethanol. Its absorbance was measured at 555 nm after 30 min¹⁵.

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