Pure & Appl. Chem., Vol. 55, No. 7, pp. 1231–1238, 1983.
Printed in Great Britain.

0033-4545/83 $3.00+0.00
Pergamon Press Ltd.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ANALYTICAL RADIOCHEMISTRY AND NUCLEAR MATERIALS*

METHODS FOR THE DETERMINATION OF FISSILE AND FERTILE ELEMENTS: BASIC DATA OF INTEREST FOR THE SPECTROPHOTOMETRIC DETERMINATION OF THORIUM

Prepared for publication by

M. SANKAR DAS (assisted by B. L. RAO)

Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India

*Membership of the Commission for the period 1981–83 is as follows:

Chairman: E. STEINNES (Norway); *Secretary:* E. A. SCHWEIKERT (USA); *Titular Members:* M. DE BRUIN (Netherlands); M. B. A. CRESPI (Argentina); F. LUX (FRG); *Associate Members:* L. GÓRSKI (Poland); J. HISLOP (UK); L. KOSTA (Yugoslavia); K. H. LIESER (FRG); B. F. MYASOEDOV (USSR); M. SAKANOUE (Japan); M. SANKAR DAS (India); N. E. WHITEHEAD (New Zealand); *National Representative:* N. SAITO (Japan).

METHODS FOR THE DETERMINATION OF FISSILE AND FERTILE ELEMENTS: BASIC DATA OF INTEREST FOR THE SPECTROPHOTOMETRIC DETERMINATION OF THORIUM

A proven alternate source of energy accessible to mankind is nuclear. To sustain this technology and to develop the future generation of power reactors - the fast breeders - extensive analytical support throughout the fuel cycle is needed. Such a programme has to be comprehensive and must include the development of methods for the determination of the fissile and fertile elements over four decades of concentration as needed from prospecting to the final assay of the pure products.

The IUPAC Commission on Analytical Radiochemistry and Nuclear Materials, while reviewing the analytical chemistry of uranium and thorium note the following:

1. One of the primary sources of information viz., the *Annual Reviews of Analytical Chemistry*, does not cover uranium and thorium.

2. The methods of analysis of uranium, a natural fissile element, is covered by a series of special publications (ref. 1-4), but the main sources for the analytical chemistry of thorium (ref. 5-10) have not been reviewed in recent years.

For these reasons the Commission decided that the basic data relevant for the development of the different methods of analysis of thorium be compiled. The present one covers the spectrophotometric method of determination of thorium.

A very large number of chromogenic reagents for thorium have appeared in literature. The present compilation lists those reagents reported from 1967 through April 1981 but not covered by the major literature sources.

The data are presented in Table 1; some further explanation of the columns is given hereunder:

Column 1: The names of the reagents are as they appear in the original publications which should be consulted for further information. A number of these reagents are also listed in *Handbook of Analytical Chemistry* by Meites (ref. 11).

Column 4: The number in brackets refers to the wavelength of absorption at which ε ($cm^{-1}.mol.dm^{-3}$) is reported for the complex.

Column 5: The number in this column is the upper limit of concentration upto which obedience to Beer's Law is reported in the relevant references. If the coloured species is extracted, the name of the organic solvent is indicated in brackets.

Column 6: For conciseness, only the name of the first author of the publication is included in this compilation. The cross references, (Column 7) are from *Chemical Abstracts* and *Analytical Abstracts*, abbreviated as *C.A.*, and *A.A.*, respectively.

GENERAL COMMENTS

1. Spectrophotometric methods continue to be important for the determination of thorium in solution in view of the poor sensitivity of atomic absorption spectrometry, which is rapidly replacing molecular absorption methods for elemental analysis.

2. The reagents have molar absorption coefficients ranging from 0.0103 to 13 x $10^4 cm^{-1}.mol.dm^{-3}$. Thorium may be determined by using these reagents at levels from 0.6 to about 200 µg/ml.

3. Among the fifty-four reagents listed in this compilation, those with arsenazo group are more frequently used and show higher selectivity. They also allow the determination of thorium in strong acid media. Even with these reagents, the presence of excessive concentrations of trivalent and quadrivalent ions, such as ferric or zirconium, lead to interference. Hence methods of determination of thorium, particularly at microgram amounts, require extensive separations. Among the methods, the sequential use of two anion exchange columns involving nitrate and chloride systems provide the best results.

Table 1. Data of Interest for the Spectrophotometric Determination of Thorium

Reagent	Empirical composition	pH	$\varepsilon \times 10^{-4}$ (λ in nm)	Upper limit of conc. µg/ml	Reference	
					Author and journal	Abstract
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1. Carmine Red	1:4	2.5	0.87 (560)	5.2	Eswaranarayana,N., *Z. Anal. Chem.*, 1955, 146, 107.	*A.A.*,1955, 2, 2691.
2. *o*-Carboxy phenylazo chromotropic acid	2:3	3	2.1 (590)	8	Majumdar, A.K., *Z. Anal. Chem.*, 1960, 174, 269.	*A.A.*,1960, 7, 5203.
3. Solochromate Fast Red	1:4	0.1M HCl	1.4 (490)	20	Korkisch, J., *Anal.Chem.*, 1961, 33, 1930.	*C.A.*,1962, 56, 4097b.
4. Sodium alizarin-3-sulfonate (Alizarin Red S)	1:2	3.2 - 8.0	0.40 (520)	16.7	Sinha, S.N., *Z. Anal. Chem.*, 1963, 195, 416.	*A.A.*,1964, 11, 3050.
5. Acid Alizarin Black SN	1:2	4.2	2.8 (600)	2.8	Kusakul, P., *Anal. Chim.Acta.*, 1965, 32, 301.	*C.A.*,1965, 62,12437f.
6. 3-Methyl galangin	1:1	2.6	4.73 (400)	13	Katyal, M., *Indian J. Chem.*, 1965, 3, 281.	*C.A.*,1965, 63,10983e.
7. *p*-Nitrophenyl azochromotropic acid (a)	1:2	3.5 - 6.5	(550)	16.6	Sangal, S.P., *Bull. Chem. Soc., Jpn.*, 1965, 38, 141.	*C.A.*,1965, 62, 9748e.
(b)	1:1	2.3 - 3.0	2.7 (580)		Toei, K., *Bull. Chem. Soc., Jpn.*, 1967, 40, 2085.	*C.A.*,1968, 68, 81821x.
8. Schiff base derived from 1-amino-8-naphthol-3,6-disulfonic acid and salicylaldehyde	1:2	3.2 - 5.2	0.7 (450)	95	Poddar, S.N., *Indian J. Chem.*, 1965. 3 (9), 407.	*C.A.*,1966, 64, 4253f.
9. Oxine		8.0 - 8.3	1.0 (390)	20 (5% isopentanol in $CHCl_3$)	Goto, K., *Anal. Chem.*, 1966 38, 493.	*A.A.*,1967, 14, 3894.
10. Malanoxetin	1:1	2	2.1 (420)	7	Katyal, M., *Curr. Sci.*, 1966, 35 (15), 388.	
11. Molybdophosphoric acid (a)		3	3.3 (690)	20 (via molybdenum blue)	Bryan, L.M., *Anal. Chem.*, 1967, 39, 1706.	*C.A.*,1967, 68, 1845c.
(b)	1:1:12	1	(350)	7 (n-butyl acetate)	Murata, K., *Anal.Chim.Acta.*, 1969, 48, 349.	*C.A.*,1970, 72,18219z.

A.A. = Analytical Abstracts; *C.A.* = Chemical Abstracts

Table 1 (contd.)

Reagent	Empirical composition	pH	$\varepsilon \times 10^{-4}$ (λ in nm)	Upper limit of conc. µg/ml	Reference	
					Author and journal	Abstract
(1)	(2)	(3)	(4)	(5)	(6)	(7)
12. Brompyrogallol Red (a)	1:1	2	2.5 (590)	4	Vasilenko, V.D., *Zh. Anal. Khim.*, 1967, 22, 1818.	*C.A.*, 1968, 68, 65428u.
(b)	1:2	5	6.3 (630)	2.4	idem	
(c)	1:2	5.6 - 5.9	5.1 (645)	4.2	Tonosaki, K., *Bull. Chem. Soc., Jpn.*, 1969, 42,456.	*C.A.*, 1969, 70, 84024s.
(d)		4-5	5.3 (650)		Shanya, M.V., *Kompleksoobrazov. Mezhmol. Vzaimodeistvie Soosazhed. Nekot. Sist.*, 1970, 157-64, Dnepropetrovsk.	*C.A.*, 1972, 76, 10022s.
13. Arsenazo dianilide	1:2	1.2M HCl	36 (654)	(butanol)	Budesinsky, B., *Talanta*, 1967, 14, 523.	*C.A.*, 1967, 66, 121814q.
14. Arsenazo III (a)		0.1M HCl	4.93 (660)	2 (HDEHP)	Cerrai, E., *Anal. Chim. Acta.*, 1967, 37, 295.	*C.A.*, 1967, 66, 111273y.
(b)		≥6M HCl	8.77 (660)	0.6 (HDEHP)	-do-	
(c)	1:1	11.3M HNO_3			Borak, J., *Talanta*, 1970, 17, 215.	*C.A.*, 1970, 72, 117320g.
(d)		8M HCl	12.4 (655)		Ref. 12(d)	-
15. Anthrapurpurin			(540)	21	Captain, F., *Ars. Pharm.*, 1967, 8, 399.	*C.A.*, 1968, 69, 15904w.
16. Quinalizarin (a)		4.7	(570)	10	Barra, F.T., *Rev. Real. Acad. Ciene. Exactas, Fis., Natur., Madrid*, 1967, 61, 827.	*C.A.*, 1968, 69,24277w.
(b)	1:1	3.5		10 (butanol)	Dragulescu, C., *Rev. Roum. de Chem.*, 1970, 15, 563.	*A.A.*, 1972, 22, 80.
17. Murexide	1:1	8-9	1.8 (470)	20	Malik, W.U., *J. Less Common Metals*, 1968, 16, 385.	*C.A.*, 1969, 70, 8646f.
18. N,N-Bis(2-hydroxy-5-sulfophenyl)-C-cynoformazon	1:1		1.5	30	Furukawa, M., *Nagoya Kogyo Gijutsu Shikensho Hokoku*, 1968, 17, 161.	*C.A.*, 1969, 71, 9299c.

Table 1 (contd.)

Reagent	Empirical composition	pH	ε x 10^{-4} (λ in nm)	Upper limit of conc. µg/ml	Reference	
					Author and journal	Abstract
(1)	(2)	(3)	(4)	(5)	(6)	(7)
19. Kaempferol	1:1	2.5	2.1	8	Garg, B.S., *Indian J. Chem.*, 1968, 6, 334.	*C.A.*, 1968, 69, 70614b.
20. Robinetin	1:1	3.0	23 (415-430)	4.8	idem	idem
21. Methyl Thymol Blue (MTB) + 1,3-Diphenyl guanidine (DPG)	1:2:4 Th:MTB: DPG	2.5-3	6.6 (590)	3	Otomo, M., *Nippon Kagaku Zasshi*, 1968, 89, 503.	*C.A.*, 1968, 69, 32756s.
22. Xylenol Orange + 1,3-Diphenyl-guanidine		2.5-3.6	9.3 (578)	0.83 (butanol)	Otomo, M., *Nippon Kagaku Zasshi*, 1968, 89, 1087.	*C.A.*, 1969, 70, 73983c.
23. Chromeazurol S (CAS) + Cetyl-trimethyl ammonium chloride	1:4 Th:CAS	5.6 - 6.1	17.4 (631)	0.8	Shijo, Y., *Bunseki Kagaku*, 1969, 18, 469.	*C.A.*, 1969, 71, 98040b.
24. Methyl Thymol Blue (a)	1:2	9-10	2.9 (535)	2.8	Adams, J., *Talanta*, 1969, 16, 1596.	*C.A.*, 1970, 72, 96382m.
(b)	1:2	5	5.4 (580)		Vasilenko, V.D., *Zh. Anal. Khim.*, 1965, 20, 636.	*A.A.*, 1967, 14, 76.
(c)		4-5	5.3 (585)		vide Ref. 12(d).	
25. Quercetin	1:2	3	(425)		Babko, A.K., *Ukr. Khim. Zh.*, 1969, 35, 292.	*C.A.*, 1969, 71, 9404h.
26. 4-(2-Thiozolazo)-resorcinol	1:3	6.8 - 8.5	3.15 (585)	3.8	Sakai, T., *Bull. Chem. Soc., Jpn.*, 1969, 42, 2718.	*C.A.*, 1970, 72, 38583s.
27. Solochrome Azurine B.S.	1:1	4.0 - 5.5	1.3 (600)	30	Sharma, C.L., *Z. Anal. Chem.*, 1970, 250, 383.	*C.A.*, 1970, 73, 72747d.
28. *o*-Cresolphthalexon S	1:1	1.5 - 2.2	2.95 (565)	9	Cherkesov, A.I., *Ref. Zh. Khim.*, 1971, Abst.No.7, G.22.	*C.A.*, 1972, 121159m.
	1:2	3-6	2.43 (555)			
29. 5,7-Dibromo-8-hydroxy quinoline (DBO) and Rhodamine S (RhS)	1:5:1 Th:DBO: RhS			11 (benzene)	Mishchenko, V.T., *Zh. Anal. Khim.*, 1970, 25, 1533.	*C.A.*, 1971, 74, 19087.
30. 5,7-Dinitro oxine (DNO) and Rhodamine B (RhB)	1:4:1 Th:DNO: RhB	4.5	10.5 (559)	(benzene)	Toei, K., *Nippon Kagaku Zasshi.*, 1971, 92, 731.	*C.A.*, 1971, 75, 155415m.
31. Phthalexon S	1:1	2	2.72 (535)	9	Cherkesov, A.I., *Ftaleksony*, 1970, 165-72, Saratov	*C.A.*, 1972, 76, 121158k.
	1:2	5	3.65 (545)		idem	idem

Table 1 (contd.)

Reagent	Empirical composition	pH	ε x 10^{-4} (λ in nm)	Upper limit of conc. µg/ml	Reference	
					Author and journal	Abstract
(1)	(2)	(3)	(4)	(5)	(6)	(7)
32. Thymol Phthalexon S	2:1	1.5	3.1 (590)		Cherkesov, A.I., *Zh. Anal. Khim.*, 1971, 26, 755.	*C.A.*, 1971, 75, 26068h.
	1:1	4-6	4.03 (590)	8		
33. 1'-(1-Phenyl-3-methyl-5-oxo-2-pyrazoline-4-ylazo)-2'-hydroxy-5'-benzosulfonate	1:2	5-6	1.3 (480)	14	Patroescu, C., *Chim. Anal.*, 1971, 1, 111.	*C.A.*, 1972, 76, 30387t.
34. Rufigallic acid		4.3	(540)	12	Captain, F., *Rev. Soc. Venez. Quin.*, 1971, 8, 33.	*C.A.*, 1973, 78, 168195b.
35. Chromotropic acid azodyes of pyridine series	1:1	5.3	0.069 (560)	22.4	Majumdar, A.K., *Talanta*, 1971, 18, 968.	*Nucl. Sci. Abstr.*, 26, 4189.
36. Methyl xylenol blue with Cetyl pyridinium chloride		1.6	(580)	≤230	Enoki, T., *Bunseki Kagaku.*, 1972, 21, 87.	*C.A.*, 1972, 76, 107581m.
37. Dithizone	1:2	6.7 - 9.7	(500)	3.5	Malik, W.U., *Z. Anal. Chem.*, 1972, 258, 124.	*C.A.*, 1972, 76, 107595u.
38. 3-Nitroso-4-hydroxycoumarin	1:1	4.5-6	0.0103 (419)	200	Manku, G.S., *Mikrochim. Acta.*, 1972, (6), 811.	*C.A.*, 1973, 78, 66603r.
39. Purpurin	1:1	2.5-3	(533)	0.51 (butanol)	Dragulescu, C., *Rev.Roum.de Chim.*, 1973, 18, 43.	*C.A.*, 1973, 78, 92086u.
40. Chlorophosphonazo III (a)	1:2	2-3M HCl	13 (690)	1.5 (3-methyl-1-butanol)	Yamamoto, T., *Anal.Chim.Acta.*, 1973, 63, 65; also JEARI-M-5426, 1973.	*C.A.*, 1973, 78, 66578m. *C.A.*, 1975, 82, 129940d.
(b)		6N H_3PO_4	3.59 (685)	4	Lukin, A.M., *Zavod. Lab.*, 1973, 39, 1174.	*C.A.*, 1974, 80, 55531f.
41. Chromeazurol S(CAS) + Cetyl trimethyl ammonium bromide (CTAB)	1:5:20 Th:CAS:CTAB	4.5	14.6 (635)	1.14	Evtimova, B., *Anal.Chim.Acta.*, 1974, 68, 222.	*C.A.*, 1974, 80, 78064v.
42. Solochrome Red B		3.5	(560)	45	Khalifa, H., *Z. Anal. Chem.*, 1974, 272, 364.	*C.A.*, 1975, 82, 132528f.
43. Glycine Cresol Red(GCR) + Cetyl trimethyl bromide (CTAB)	1:2:4 Th:GCR:CTAB	4.5	5.2 (560)	3	Golentovskaya,I.P. Deposited Doc., VINITI, 1974, 1856-74.	*C.A.*, 1977, 86, 182551m.
44. *o*-Cresolphthalexon S (OCP) + Benzothiuronium (BT)	1:2:2 Th:OCP:BT	3	6.2 (580)	11	Golentovskaya,I.P. Deposited Doc., VINITI, 1974, 489-74.	*C.A.*, 1977, 86, 182529k.

Table 1 (contd.)

Reagent	Empirical composition	pH	ε x 10^{-4} (λ in nm)	Upper limit of conc. µg/ml	Reference	
					Author and journal	Abstract
(1)	(2)	(3)	(4)	(5)	(6)	(7)
45. Glycine Thymol Blue	1:2 1:3		(450)	9.2 4.6	Akmedli, M.K., *Azerb. Khim. Zh.*, 1975, (2), 94.	*C.A.*, 1976, 85,86662g.
46. Morin	1:3	1.9	7.3 (420)	2.3 (iso-pentanol)	Blank, A.B., *Zh.Anal.Khim.*, 1975, 30, 1116.	*C.A.*, 1975, 83,201488c.
47. (a) Gentian Violet + Oxine (b) Gentian + 5,7-dibromo oxine		3.5	2.0 (597)	10 (benzene) 100 (benzene)	Kolesnik, R.I., *Fiz-Khim.Metody, Anal. Kontrolnaya Proizvod*, 1975, pp. 94.	*C.A.*, 1977, 87,145257r.
48. Lawsone semicarbazone	1:1	2-3	0.38 (560)	3.7	Nejkar, A.D., *J. Univ. Poona, Sci. Technol.*, 1976, 48, 285.	*C.A.*, 1977, 86,149995m.
49. *p*-Dimethylarsenazo III	1:2	5M HCl	13 (690)		Luk'yanov, V.F., *Zavod Lab.*, 1976, 42, 1302.	*C.A.*, 1977, 86,100429r.
50. Semimethyl Xylenol Blue	1:2	2.9 - 3.4	5.97 (559-564)	2.2	Weda, J., *Nippon Kagaku Kaishi*, 1977, (3), 350.	*C.A.*, 1977, 87,77848m.
51. Glycine Cresol Red + Cetylpyridinium bromide		3.6 - 4.1	7.6 (546-551)	1.2	Weda, J., *Kanazawa Daigaku Kyoikugakubu, Shizen Kagaku Hen*, 1977, 26, 5.	*C.A.*, 1979, 91,203803r.
52. Xylenol Orange + Cetyl trimethyl bromide		2.5	5.5 (600)	4	Ramakrishna, T.V., *Talanta*, 1979, 26, 499.	*C.A.*, 1979, 91,203703h.
53. Sodium 4,8-diamino-1,5-dihydroxy anthroquinone-2,6-disulfonate	1:1	3.5	(685)	22.5	Navas, A., *An. Quim.*, 1979, 75, 511.	*C.A.*, 1980, 92,14767s.
54. 2-(2-Thiazolylazo)-5-dimethylamino phenol + Cetyl pyridinium chloride	1:3	4.3 - 4.8	8.6 (570)	2.4	Chikao, T., *Bunseki Kagaku*, 1979, 28(2),754.	*C.A.*, 1980, 92,103702j.

4. Most of the free ligands show residual absorbances at the optimal pH of measurements and the wave length of absorbance of the corresponding complex; a feature which affects the low limit of determination of thorium.

5. Many of the reagents of good selectivity form coloured lakes which have a tendency to precipitate out from the solution, thus affecting the time-dependent stability of the system; a factor of importance for differential spectrophotometric determinations of improved precision.

6. The stability of some of the systems has been improved to some extent by the use of surfactants or by extraction with liquid anion exchangers, such as Di-(2-ethyl hexyl) phosphoric acid (HDEHP).

The Commission would appreciate if its attention is drawn to any omission which the reader would find in this report.

REFERENCES

1. Analysis of Essential Nuclear Reactor Materials, Ed. Rodden, C.J., Divn. of Tech. Inf. U.S.A.E.C. (1964).
2. Analytical Methods in the Nuclear Fuel Cycle, Proceedings of a Symposium, Int. At. Energy Agency, Vienna (1972), pp. 586.
3. Analytical Chemistry of Nuclear Fuels, Proceedings of a Panel, Int. At. Energy Agency, Vienna (1972), pp. 221.
4. Annual Book of ASTM Standards, Part 45, Nuclear Standards, American Soc. for Testing and Materials, Philadelphia, Penn. USA (1980).
5. Progress in Nuclear Energy Series IX, Vol. I, Ed. Kelly, M.T., Chapter 'Analysis of Thorium', Banks, C.V., Pergamon Press (1959).
6. The Radiochemistry of Thorium, Hyde, E.K., NAS-NS 3004, U.S.A.E.C. (1960).
7. Treatise on Analytical Chemistry, Ed. Kolthoff, I.M., and Philip J. Elving, Part II, Vol. 5, Chapter 'Thorium', Grimaldi, F.S., Interscience Publishers, New York - London (1961).
8. International Series of Monographs on Analytical Chemistry, Ed. Belcher, R., and Gordon, L.; Analytical Chemistry of Thorium, Ryabchikov, D.I., and Gol'braikh, E.K., translated by Norris, A.D., Pergamon Press, Oxford (1963).
9. Arsenazo III (in Russian), Savinn, S.B., Atomizdat, Moscow (1966); also Talanta 8, (1961), 673.
10. Handbook of Analytical Chemistry of Rare Elements, Busev, A.I., Tiptsova, V.G., and Ivanov, V.M., translated by Schmorak, J., Ann Arbor-Humphrey Science Publishers, Ann-Arbor (1970).
11. Handbook of Analytical Chemistry, Meites, L., McGraw-Hill, New York (1963).