

none, commonly known as plumbagin. In the present note the stability constants of the metal chelates of plumbagin with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) are reported in 75% (v/v) ethanol-water mixture at 30° and 0.1 ionic strength.

Plumbagin was isolated from the roots of the plant *Plumbago zeylanica* following the method of Roy *et al.*³. Standard solution of plumbagin was prepared in doubly distilled ethanol. The solutions of metal ions were prepared and estimated by the standard method⁴. All the pH measurements were carried out on an Elico digital pH meter model L1-120 fitted with a combined electrode type CN-67 (accuracy ± 0.01). The pH values were corrected in aquo-organic mixtures using the method of Van Uitert and Haas⁵ (correction factor, -0.33 pH units).

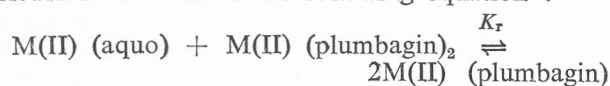
Titration of the following solutions (total volume 50 ml) were carried out against CO₂-free NaOH ($5 \times 10^{-2} M$); (i) HNO₃ ($2 \times 10^{-3} M$) + KNO₃ ($1 \times 10^{-1} M$), (ii) HNO₃ ($2 \times 10^{-3} M$) + plumbagin ($1 \times 10^{-3} M$) + KNO₃ ($1 \times 10^{-1} M$), and (iii) HNO₃ ($2 \times 10^{-3} M$) + plumbagin ($1 \times 10^{-3} M$) + M(II) (aquo) ($2.5 \times 10^{-4} M$) + KNO₃ ($1 \times 10^{-1} M$). Plumbagin was taken in four-fold excess as compared to the metal ion to avoid hydrolysis of the metal ion.

From the pH titration curves, the values of n_A , n and pL were obtained adopting the Irving-Rossotti technique⁶. The pK_a value of plumbagin obtained

from the plot of $\log \left(\frac{\bar{n}_A}{1-\bar{n}_A} \right)$ vs pH was found to be 9.95 ± 0.02 . The maximum value of \bar{n} obtained in the pH region where hydrolysis of metal ion is negligible is between 1.5 and 2.0 revealed that metal-ligand ratio in the complex is 1:2. The metal-ligand stability constants were obtained from the formation curves (\bar{n} vs pL), by plotting pL vs $\log \left(\frac{1-\bar{n}}{n} \right)$ for $\log K_1$ and pL vs $\log \left(\frac{2-\bar{n}}{n-1} \right)$ for \log

K_2 and also through other computational techniques⁷ like least-square method and correction-term method. The average $\log K$ values are noted in Table 1. The $\log K$ values (Table 1) follow the order: Cd(II) < Zn(II) < Cu(II) > Ni(II) > Co(II) > Mn(II), which is in accordance with the Irving-William order suggesting that plumbagin is a weak field ligand. The observed trend in $\log K$ values of Zn(II) > Ni(II) can be understood by considering that plumbagin, being an oxygen donor and weak field ligand, forms stronger complexes with ligand field insensitive Zn(II) as compared to the ligand field sensitive Ni(II). The $\log K$ values of Cd(II) chelates are significantly smaller than those of Zn(II) chelates, probably due to lower ionic potential.

The stabilization effects in these chelates can be discussed in terms of the following equation:



Statistically expected $\log K_r$ value⁸ is 0.90. The $\log K_r$ values (Table 1) obtained for Ni(II), Co(II) and Mn(II) chelates tally with the statistical value within reasonable limits. The $\log K_r$ value for Cu(II) is

TABLE 1—STABILITY CONSTANTS OF THE CHELATES OF Cu(II), Ni(II), Co(II), Mn(II), Zn(II) AND Cd(II) WITH PLUMBAGIN IN 75% (v/v) ETHANOL-WATER MIXTURE AT 30° AND 0.1 IONIC STRENGTH

Metal ion	$\log K_1$	$\log K_2$	$\log K_r$
Cu(II)	8.41	6.82	1.59
Ni(II)	6.02	4.94	1.08
Co(II)	5.76	4.70	1.06
Mn(II)	5.00	4.25	0.75
Zn(II)	6.21	5.90	0.31
Cd(II)	5.26	4.88	0.38

too high and those of Zn(II) and Cd(II) chelates are too low, indicating that 1:2 chelates are favoured over 1:1 chelates in Zn(II) and Cd(II) chelates, while 1:1 chelate is favoured in the case of Cu(II). The 1:2 chelate of Cu(II) possessing distorted octahedral configuration due to Jahn-Teller effect is probably de-stabilized by the steric repulsion induced by the large size of plumbagin.

The authors wish to thank Dr. T. Sundara Ramaiah, Reader in Chemistry, Nizam College for his assistance in the isolation of the ligand. One of the authors (B. V. Rao) is grateful to the UGC, New Delhi for the award of a Teacher Fellowship under the faculty improvement programme.

References

1. THOMSON, R. H., *Naturally occurring quinones* (Butterworths London), 1957, 97.
2. JOSHI, C. R. & KULKARNI, B. A., *J. univ. Poona sci. Technol.*, **46** (1974), 33.
3. ROY, A. C. & DUTT, S., *J. Indian chem. Soc.*, **5** (1928), 419.
4. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longman, London), 1975.
5. VAN UITER, L. G. & HAAS, C. G., *J. Am. chem. Soc.*, **75** (1953), 451.
6. IRVING, H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
7. IRVING, H. M. & ROSSOTTI, H. S., *J. chem. Soc.*, (1953), 3397.
8. TING, POI & NANCOLLAS, H., *Inorg. Chem.*, **11** (1972), 2414.

Photometric Determination of Fluoride Using Various Metal Oximates

D. VENKATA REDDY* & V. KRISHNA REDDY

Department of Chemistry, SVU Autonomous Post-graduate Centre, Anantapur 515 003

Received 3 March 1980; revised and accepted 11 August 1980

The bleaching effect of fluoride ion on uranium(VI) complexes of salicylaldoxime (SAO), 2-hydroxy-1-naphthaldoxime (OHNAO), peonol oxime (MRPO) and 2-hydroxy-5-methylpropiofenone oxime (HMPOX) at pH 6.0 and on iron(III) complex of OHNAO at pH 2.5 and MRPO and HMPOX complexes at pH 3.0 has been utilised for the determination of fluoride ion in microgram quantities.

THOUGH a large number of sensitive spectrophotometric methods are available¹⁻⁵ for the

determination of fluoride, most of them suffer from the interference of manganese(II), chloride, sulphate, calcium and magnesium ions. This prompted us to develop a photometric method for the determination of fluoride. This is based on the bleaching effect of fluoride ion on uranium(VI) and iron(III) complexes.

Uranium(VI) formed soluble orange-red coloured complexes with salicylaldoxime (SAO), 2-hydroxy-1-naphthaldoxime (OHNAO), peonol oxime (MRPO) and 2-hydroxy-5-methyl propiophenone oxime (HMPOX) in the pH range 5-11. Iron(III) formed a bluish-green coloured complex with OHNAO and bluish-violet coloured complexes with MRPO and HMPOX in the pH range 1-3.5. Addition of fluoride in microgram quantities to these metal oximates resulted in the proportional decrease of the absorbance of uranium(VI) chelates at pH 6.0 and of iron(III) chelates at pH 3.0.

Alcoholic solutions (0.1 and 0.05 M) of the oximes SAO, OHNAO, MRPO and HMPOX were used. Uranyl solution (0.01 M) was prepared by dissolving 1.2554 g of uranyl nitrate (BDH, AR) in distilled water. Iron(III) solution (5×10^{-3} M) was prepared by dissolving ferric ammonium sulphate (M & B) in distilled water containing sulphuric acid.

Sodium fluoride (0.221 g, AR) was dissolved in distilled water and made upto 500 ml. Sodium acetate-acetic acid buffer solution of pH 6.0 and sodium acetate-hydrochloric acid buffers of pH 2.5 and 3.0 were used.

Recommended procedure — In a number of volumetric flasks of 25 ml capacity, salicylaldoxime (1 ml), buffer solution (12 ml) of pH 6.0 and uranyl nitrate (1 ml) were added. Various aliquots of fluoride solution were added to these flasks and the contents made upto the mark with distilled water. The absorbances of these solutions were measured at 400 nm against water as blank. A linear plot was obtained when the absorbance values were plotted against the amount of fluoride added, showing the usefulness of the method for the determination of fluoride.

Similar procedures were adopted for the determination of fluoride using uranium(VI) and iron(III) oximates of OHNAO, MRPO and HMPOX. While using Fe(III) oximates the pH was maintained at 2.5 and 3.0.

The results in Table 1 indicate that the bleaching effect of fluoride over iron(III)-peonol oxime complex and iron(III)-HMPOX complex is more sensitive than in other cases. Therefore, fluoride in very low concentrations (1-5 ppm) could be determined employing these metal oximates. This may be due to greater stability of iron(III)-fluoride complex compared to the corresponding metal-oximates. This opinion is further strengthened by the fact that the instability constants of the oximates are far greater in magnitudes compared to uranium(VI)-fluoride and iron(III)-fluoride⁶ complexes (Table 2).

Salicylaldoxime forms a stronger complex with iron(III) than the fluoride iron. Hence iron(III)-SAO complex could not be employed. The uranium(VI) oximate solutions are stable for more than 3

TABLE 1 — DETERMINATION OF FLUORIDE

Metal oximate	pH	Fluoride determined (in ppm)
Uranium(VI)-SAO	6.0	10-120
Uranium(VI)-OHNAO	6.0	4-24
Uranium(VI)-MRPO	6.0	4-20
Uranium(VI)-HMPOX	6.0	4-20
Iron(III)-OHNAO	2.5	2-8
Iron(III)-MRPO	3.0	1-5
Iron(III)-HMPOX	3.0	1-5

TABLE 2 — INSTABILITY CONSTANTS OF METAL OXIMATES

Metal oximate	K_{inst}
Uranium(VI)-SAO	8×10^{-4}
Uranium(VI)-OHNAO	4×10^{-2}
Uranium(VI)-MRPO	7.31×10^{-6}
Uranium(VI)-HMPOX	5.72×10^{-3}
Iron(III)-OHNAO	2×10^{-3}
Iron(III)-MRPO	2.72×10^{-6}
Iron(III)-HMPOX	2.5×10^{-3}

U(VI)-fluoride : $K_{inst.} = 3 \times 10^{-8}$
 Fe(III)-fluoride : $K_{inst.} = 8.7 \times 10^{-13}$

days. However, iron(III) oximate solutions are found to be stable for 2 to 3 hr.

The interference of various ions which are generally found in association with fluoride has been studied. Sodium, potassium, calcium, barium, strontium, magnesium, zinc, thorium(IV), chloride, bromide, iodide, sulphate, nitrate and acetate did not interfere when present in more than 2000-fold excess. Manganese(II) interfered when it was present in four-fold excess with uranium(VI) oximates, but its interference was absent even when present in 1000-fold excess when iron(III) oximates were employed. Copper(II), nickel(II), cobalt(II) and titanium(IV) interfered due to the formation of coloured precipitate. Carbonate, arsenate and aluminium could be tolerated upto four-fold excess. Citrate and tartrate interfered when they are present in two-fold excess.

The method developed using iron(III)-peonol oximate was employed for the determination of fluoride content in drinking water. The water was first freed from carbonate by boiling with dilute hydrochloric acid. The pH of the water was then adjusted to 3.0 with sodium acetate and the fluoride content determined using iron(III)-peonol oxime complex. The results by the present method are comparable with those obtained using standard zirconium-alizarin red-S method.

The authors are grateful to the CSIR, New Delhi for the award of a junior research fellowship to one of them (V. K. R.). The authors are also thankful to Prof. S. Brahmaji Rao for his interest in the work.

References

- BUMSTEAD, H. E. & WELLS, J. C., *Analyt. Chem.*, **24** (1952), 1595.
- KAMADA, M., ONISHI, T. & OTA, M., *Bull. chem. Soc., Japan*, **28** (1955), 148.

3. CURRY, R. C. & MELLON, M. G., *Analyt. Chem.*, **28** (1956), 1567.
4. SZABÓ, Z. G., BECK, M. T. & TOTH, K., *Mikrochim. Acta*, (1958), 181.
5. UEDA, I., *Shika Igaku*, **32** (1969), 726; *Chem. Abstr.*, **73** (1970), 51984.
6. YTSIMIRSKII, K. B. & VASILEV, V. P., *Instability constants of complex compounds* (Van Nostrand, Princeton, New Jersey), 1960, 130.

Manganese(IV) as an Analytical Reagent for Determination of Tellurium

S. BHANOJEE RAO & B. R. SANT*
Regional Research Laboratory, Bhubaneswar

Received 19 April 1980; revised and accepted 6 June 1980

A simple and rapid method for the estimation of tellurite using excess manganese(IV) sulphate solution is reported. Manganese(IV) is reduced to manganese(III) and the excess of the reagent is titrated with standard iron(II) solution.

TELLUROUS acid and tellurites are not easily oxidised and most of the methods for their estimation are very old and involve addition of excess oxidant and back titration. Recently Mandal and Sant^{1,2} reported the preparation and utilization of manganese(IV) sulphate as an oxidant. Our preliminary experiments revealed that Te(IV) is completely oxidised to Te(VI) in sulphuric acid medium.

Manganese(IV) sulphate solution was prepared and standardised as described earlier¹. For the preparation of tellurite solution, potassium tellurite was dissolved in 0.01 N potassium hydroxide and standardised with ceric sulphate.

All other reagents used were of AR grade.

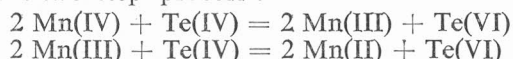
TABLE 1 — ESTIMATION OF TELLURITE

Sulphuric acid molarity	Tellurite(M)	
	Taken	Found
6	0.07144	0.07144
8	0.07144	0.07144
10	0.07144	0.07144
12	0.07144	0.07144
14	0.07144	Erratic
16	0.07144	Erratic
10	0.1169	0.1169
10	0.1754	0.1754
10	0.05845	0.0584

Procedure—To an aliquot of tellurite solution sulphuric acid was added to maintain an overall molarity of 8-10. To this was added a known excess of manganese(IV) sulphate solution. After 15 min at room temperature the excess oxidant was titrated with standard iron(II) solution using ferroin as indicator. One millilitre of 0.1 N Mn(IV) sulphate solution corresponds to 6.38 mg tellurium.

Typical results for the estimation of tellurium are given in Table 1.

The oxidation of tellurium(IV) by manganese(IV) is a two step process :



The first reaction is complete within 5-10 min at ambient temperature and the second reaction is slow and is not complete even after 6 hr. However, when excess of manganese(IV) is present only the first reaction takes place enabling the precise estimation of Te(IV). The principal advantage of the method is its simplicity and accuracy.

References

1. MANDAL, S. K. & SANT, B. R., *Talanta*, **23** (1976), 485.
2. MANDAL, S. K. & SANT, B. R., *Indian J. Chem.*, **19A** (1980), 389.