TABLE I

The proton-ligand stability constant of Hydroxyl group of 1-naphthol and other substituted naphthols at 35° C and an ionic strength $\mu = 0{\cdot}1\ M\ KNO_3$

Sl. No.	Name of the ligand	pK ± 0 02 in 50 % V/V Acetone-water	Literature Value	Reference
1.	1-Hydroxy 2-naphthoic acid	.. 11·96	14·00 in 50 % dioxane water at 30° C	6
2.	1-Naphthol	.. 10·96	9·34 in aqueous medium at 25° C	7
3.	2-Acetyl 1-naphthol	.. 10·72	13·6 in 75 % dioxane-water mixture at 25° C	8
4.	1-Hydroxy naphthalene 4 sulphonic acid (*Na* - Salt)	.. 9·81	..	..
5.	1-Amino 2-hydroxy naphthalene 4 sulphonic acid	.. 8·46	..	..
6.	2-Nitroso 1-naphthol	.. 8·16	8·90 in 50 % dioxane water at 30° C	9
7.	Nitroso - R-Salt	.. 7·71	6·94 in aqueous medium	10
8.	1-Hydroxy 2-nitrosonaphthalene 4-sulphonic acid	.. 7·16	..	..

Hence, the pK of 1-hydroxy 2-nitrosonaphthalene 4-sulphonic acid will be (10·96 — 3·95 = 7·01). The observed pK value of 7·16 for 1-hydroxy 2-nitrosonaphthalene 4-sulphonic acid fairly agrees with the predicted one.

The low pK value in nitroso-R-Salt is due to the presence of two electron withdrawing groups in ortho position to hydroxyl group. The enhanced basic character in 1-amino 2-hydroxynaphthalene 4-sulphonic acid is due to the presence of electron repelling $-NH_2$ group in ortho position and the electron withdrawing tendency of $-SO_3H$ group. The electron withdrawing tendency of $-SO_3H$ group will be much less in meta position when compared to para position.

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1. *Determination of Organic Structures by Physical Methods*, Edited by E. A. Braude and F. C. Nachod, Vol. I (Academic Press, Inc., New York), 1955, p. 567.
2. Chaberek, S. (Jr.) and Martell, A. E., *J. Am. Chem. Soc.*, 1952, 74, 5052.
3. Welcher, F. J., *Organic Analytical Reagents* (Van Nostrand Co., London), 1962, p. 324.
4. Stroughton, *J. Am. Chem. Soc.*, 1935, 57, 202.
5. Van Uitert, L. G. and Haas, C. G., *Ibid.*, 1953, 75, 451.
6. Aggett, J. and Cha-duk Kim, *Australian Atomic Energy Commission, Rep. T.M.*, 1964, p. 240.
7. Weast, R. C., *C.R.C. Hand-Book of Physics and Chemistry*, 48th Edition, 1967–68, D-90.
8. Van Uitert, L. G. and Fernelius, W. C., *J. Am. Chem. Soc.*, 1954, 76, 375.
9. Callahan, C. M., Ferneleius, W. C. and Bloch, B. P., *Analyst. Chim. Acta*, 1957, 16, 101.
10. Mandal, S. and Dey, A. K., *Revue de Chimie minerable*, t_5, 1968, p. 773.
11. Jack Hine, *Physical Organic Chemistry* (McGraw-Hill Book Company, Inc., New York), 1962, p. 100.

RESACETOPHENONE OXIME AS AN INDICATOR FOR THE TITRIMETRIC DETERMINATION OF FLUORIDE

ANALYTICAL applications of resacetophenone oxime have been reported earlier from these laboratories[1–4]. In the present communication the application of this compound in the titrimetric determination of fluoride is described.

Resacetophenone oxime reacts with iron (III) in the pH range 4·5–7·0 to form a violet colored (1 : 1) complex[3]. Ferric fluoride complex is stronger than ferric resacetophenone oxime complex and this forms the basis for the procedure described below.

Procedure.—A known volume of sodium fluoride was taken in a 100 ml pyrex conical flask, about 2·0 gm of sodium chloride was next added. The

contents were shaken well and treated with an equal volume of 95% ethanol, followed by 1 ml of the indicator solution (2% solution in 95% ethanol). It was then titrated with 0·05 N ferric chloride solution in 0·01 hydrochloric acid; the appearance of a permanent light violet color indicated the end point. The typical results are recorded in Table I.

TABLE I

Determination of fluoride with resacetophenone oxime as indicator

S.No.	Fluoride, mg taken	Fluoride, mg found	error %
1 ..	5·29	5·26	−0·56
2 ..	7·40	7·42	+0·35
3 ..	10·58	10·52	−0·56
4 ..	11·63	11·61	−0·13
5 ..	12·69	12·70	+0·04
6 ..	13·75	13·64	−0·80
7 ..	14·81	14·71	−0·67
8 ..	15·87	15·95	+0·50

Interference.—The elements usually associated with fluoride, *viz.*, chloride, iodide, bromide, borate, phosphate, perchlorate, silicate, nitrate, sulphate, nitrite, carbonate. sulphite, tartrate, oxalate, citrate, and acetate were added in 10 fold excess in each case and the titration was carried out using the same procedure. Amongst these ions borate, phosphate silicate, tartrate, acetate, citrate, oxalate and sulphite caused interference by giving rise to premature end point. Nitrite interfered only when it was present in more than 2 fold excess. Carbonate altered the pH and thus interfered; elimination of carbonate with dilute hydrochloric acid is necessary prior to the commencement of the titration.

Discussion.—Tables I and II clearly show that fluoride could be satisfactorily determined by this method when present alone and also in the presence of 10 fold excess of certain ions which are usually associated with fluorine in waters and ores.

Resacetophenone oxime can be easily prepared and recrystallised from aqueous alcohol using animal charcoal. The alcoholic solutions are fairly stable for long periods. The authors therefore consider this as a good indicator for the determination of fluoride with iron (III). Thiocyanate[5] and sodium salycilate[6] were used as indicators in the determination of fluoride with iron (III). Color change in the case of thiocyanate is not facile. sodium salycilate is a sensitive indicator, but it is necessary to maintain carefully controlled conditions for this titration. In the case of resacetophenone oxime the little acid that is usually employed in the preparation of ferric chloride (0·01 N HCl) will form the necessary pH conditions for the titration. Hence it is a simple and rapid method.

TABLE II

Effect of foreign ions in the determination of fluoride

Fluoride taken, mg	Foreign ions added (10–100 mg)	Fluoride found mg	Error %
10·35	nitrate ($NaNO_3$)	10·37	+0·19
10·35	sulphate (Na_2SO_4)	10·37	+0·19
10·35	chloride (NaCl)	10·37	+0·19
10·35	Iodide (KI)	10·37	+0·19
10·35	bromide (KBr)	10·37	+0·19
10·35	carbonate (Na_2CO_3)	10·37	+0·19
10·35	perchlorate ($KClO_4$)	10·37	+0·19

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1. Krishna Reddy, Y., *Proc. Ind. Acad. Sci.*, 1965, **61 A**, 368.
2. — and Appala Raju, N., *Ind. Jour. of Chem.*, 1972, **10**, 558.
3. Raja Reddy, G. *et al.*, *Proc. Ind. Acad. Sci.*, 1964, **59 A**, 159.
4. Mangeswara Rao, P. and Brahmaji Rao, S., *Ind. Jour. of Chem.*, 1971, **9**, 1014.
5. Sommer, L., *Chem. List*, 1953, **47**, 906; *Anal. Abs.*, 1955, **2**, 78; *Cf. C.A.*, 1954. **48**, 3848.
6. Miyahara, Y., *Botyu-Kagaku.*, 1953, **18**, 176; *Cf. C.A.*, 1954, **48**, 1199 *a*.

SYNTHESIS OF THE N-TERMINAL TETRAPEPTIDE SEQUENCE OF HUMAN FIBRINOPEPTIDE-A

FIBRINOPEPTIDE-A is released from fibrinogen during the process of blood coagulation[1]. Human fibrinopeptide-A is a hexadecapeptide with the amino acid sequence[2], Ala-Asp-Ser-Gly-Glu-Gly-Asp-Phe-Leu-Ala-Glu-Gly-Gly-Gly-Val-Arg. With a view to synthesise this hexadecapeptide by the fragment condensation, the two protected hexapeptides Boc-Glu (OBzl)-Gly-Gly-Gly-Val-Arg (NO_2)-OMe*