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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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*

corresponding to positions 11–16 and Boc-Glu (OBzl)-Gly-Asp (OBzl)-Phe-Leu-Ala-OMe corresponding to positions 5–10 have been synthesised in our laboratory[3,4]. We now wish to report the synthesis of the third fragment, the N-terminal tetrapeptide sequence, Ala-Asp-Ser-Gly.

The reaction of Z-Ala-OPCP[5] with Asp (OBzl)[6] yielded Z-Ala-Asp (OBzl) in 81·8% yield, m.p. 140–142°, $[\alpha]_D^{23}$ + 17·38° (DMF ; c. 1·5) (Found : C, 61·67 ; H, 5·63 ; N, 6·52%. $C_{22}H_{24}N_2O_7$ requires C, 61·67 ; H, 5·61 ; N, 6·54%). This was converted to the pentachlorophenyl ester, Z-Ala-Asp(OBzl)-OPCP, m.p. 175–178°, in 75% yield using the DCCI procedure. This active ester can also be obtained in 48% yield by the condensation of Z-Ala[7] with Asp (OBzl)-OPCP using the mixed anhydride method. Reaction of Z-Ala-Asp (OBzl)-OPCP with Ser-Gly (obtained by the catalytic hydrogenation of Z-Ser-Gly-OBzl[8]) led to the tetrapeptide Z-Ala-Asp (OBzl)-Ser-Gly, yield, 51%, m.p. 125–128°, $[\alpha]_D^{23}$ + 10·5° (DMF ; c, 0·95) (Found : C, 52·2 ; H, 5·7 ; N, 8·97%. $C_{27}H_{32}N_4O_{10}$. $3H_2O$ requires C, 51·90 ; H, 5·80 ; N, 8·94%). This protected tetrapeptide can also be obtained by an alternate method in which Boc-Asp (OBzl)-OPCP was reacted with Ser-Gly to furnish Boc-Asp(OBzl)-Ser-Gly, yield, 37%, m.p. 112–113°, $[\alpha]_D^{23}$ — 22·3° (DMF ; c, 2·0) (Found : C, 53·98 ; H, 6·25 ; N, 8·99%. $C_{21}H_{29}N_3O_9$ requires C, 53·94 ; H, 6·25 ; N, 8·98%). After deprotection of this tripeptide with HCl in ethyl acetate the product was made to react with Z-Ala-OPCP to yield Z-Ala-Asp (OBzl)-Ser-Gly in 51·5% yield.

A superior method of obtaining this tetrapeptide involved the conversion of Z-Ala-Asp (OBzl) to the active ester, Z-Ala-Asp (OBzl)-OSu using the DCCI procedure, yield, 85%, m.p. 105–108°, $[\alpha]_D^{23}$ — 19·61° (DMF ; c, 2·0) (Found : C, 60·37 ; H, 5·11 ; N, 8·10%. $C_{26}H_{27}N_3O_9$ requires C, 59·99 ; H, 5·18 ; N, 7·99%), followed by its condensation with Ser-Gly. The Product, Z-Ala-Asp (OBzl)-Ser-Gly, obtained in 71% yield, on catalytic reduction over 10% Pd-C in acetic acid, gave Ala-Asp-Ser-Gly AcOH, yield, 63·5%, m.p. 190–194°, $[\alpha]_D^{23}$ + 31·7° (1N HCl ; c, 0·63) (Found : C, 41·09 ; H, 6·44 ; N, 13·04%. $C_{14}H_{24}N_4O_{10}$ requires C, 41·16, H, 5·92 ; N, 13·72%).

The tetrapeptide sequence Ala-Asp-Ser-Gly is also present in the enzyme staphylococcal nuclease[9] and the dipeptide sequence -Asp-Ser- is present at the catalytic site of several proteolytic and hydrolytic enzymes like trypsin, chymotrypsin and cholinesterase[10].

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* The amino acids used, with the exception of glycine, have the L-configuration. Abbreviations : Z, benzyloxycarbonyl ; Boc, *tert*-butyloxycarbonyl ; OBzl, benzyl ester ; OPCP, pentachlorophenyl ester ; OSu, N-hydroxysuccinimide ester ; DCCI, dicyclohexyl carbodiimide.

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STABILITY OF AQUEOUS CHLORAMINE-T SOLUTIONS TO HEAT AND ULTRA-VIOLET RADIATION

Chloramine-T (p–CH_3–$C_6H_4SO_2$ NCl Na.3 H_2O), the sodium salt of p-toluene sulfochloramide has been used as a mild oxidant in volumetric analysis and as a chlorinating agent. Although the stability of aqueous solutions of chloramine-T (CAT) has been critically examined by several workers, there are controversial reports and these are summarized by Bishop and Jennings[1]. Photochemical decomposition of CAT solutions with polychromatic radiations has been reported by Eisenschimmel[2] and Carlsen[3], but no conclusive data on the mechanism are available. In the present work, some preliminary studies have been made on aqueous CAT solutions, (*i*) about their thermal stability over the temperature range 50–95° and (*ii*) on their photochemical stability at 3660 Å.

Experimental.—Chloramine-T (Rhodia) was purified by the method of Morris *et al.*[4]. An approximately decimolar stock solution was prepared and was standardized by the iodometric method. Reagent grade materials were used in preparing solutions of other compounds. All solutions were prepared in triply distilled water.

Thermal decomposition studies were carried out with aliquots of 0·053 M CAT solutions (25 or