

Spectrophotometric Determination of Traces of Fluoride Ion by Ternary Complex Formation with Zirconium and Acid Alizarin Black SN

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ABSTRACT. A simple and convenient spectrophotometric procedure has been established for the determination of small amounts of fluoride ion, based on its reaction with the chelate formed between zirconium and Acid Alizarin Black SN. Microgram amounts of fluoride (0.1-0.4 μg) can be determined with an error of less than about 2%.

Most of the spectrophotometric determinations of fluoride ion are, with two exceptions, based on the ability of fluoride to abstract the cations from coloured metal-chelates, thus liberating the free reagent (Bellack and Schouboe 1958 and Megregian 1954). Such methods tend to be unselective. The two spectrophotometric methods which differ are kinetochromic spectrophotometry (West and Cabello-Tomas 1969 and Knapp 1970) which depends on the catalytic action of fluoride ion on the zirconium-xylenol orange reaction, and the other based on the formation of strongly absorbing 1:1:1 ternary complexes (West and Leonard 1960, West and Har 1971, Einaga and Iwasaki 1981).

The aim of the present study was to establish a simple spectrophotometric determination of fluoride ion using its reaction with the metal chelate formed between AABSN and Zr. The AABSN-Zr-F complex has an absorption maximum at 605 nm with a molar absorptivity of $3.20 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.

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Experimental

Reagents

Acid Alizarin Black SN (AABSN)

A $10^{-3}M$ solution was prepared from sample supplied by Hopkins & Williams, batch No. 109900, C.I. 21725. The dye was about 60% pure. The main impurity was sodium sulphate used to isolate the dye from the aqueous medium by the "salting out" technique. Ash analyses (4) indicated the Na_2SO_4 content to be 40%.

Zirconyl Chloride, $ZrOCl_2 \cdot 8H_2O$.

A $10^{-3}M$ solution was prepared by dissolving 80.5 mg of the zirconium salt in 7.5 cm^3 of concentrated HCl and diluting to 250 cm^3 with freshly distilled water.

(The zirconium solution should be freshly prepared).

Sodium Fluoride, $10^{-4}M$.

1 cm^3 of $10^{-4}\text{ NaF} = 1.9\text{ }\mu\text{g F}^-$

Buffers

The following pH controlled solutions were prepared. $4M$ HCl, $2M$ HCl, $1M$ HCl, $0.1M$ HCl; sodium acetate/acetic acid (pH 4), $0.1M$ ammonium acetate (pH 7); ammonium chloride/ammonium hydroxide (pH 10) and 0.1 sodium hydroxide (pH 13).

All other reagents employed were of analytical reagent grade.

Instruments

1. Perkin-Elmer Model 124 recording UV/Visible Spectrophotometer.
2. Unicam SP 800 recording Spectrophotometer.

Recommended Procedure

A known volume ($1-5\text{ cm}^3$) of the standard fluoride solution ($10^{-4}M$) was transferred to a 50 cm^3 graduated flask containing 20 cm^3 of distilled water. 10 cm^3 of $10^{-3}M$ AABSN was then pipetted into the flask, and similarly 5 cm^3 of $0.1M$ HCl. The whole was mixed and 5 cm^3 of $10^{-3}M$ zirconium solution was pipetted into it with constant swirling. The solution was then made up to volume and set aside for 5 hr. The absorbance of the solution was measured at 605 nm in 1 cm cells against the blank solution which was prepared similarly but with omission of fluoride.

Analysis of Fluoride Samples

The recommended procedure was applied to determine the fluoride content in sodium fluoride and some organic samples (Table 1). The organic samples were decomposed by the oxygen - flask technique (Schoniger 1955).

Table 1. Analytical results for some fluoride sample solutions

Compound	Fluoride Calc.	(%) Found	No. of determinations
Sodium fluoride	45.25	45.30	10
P-fluorobenzoic acid*	13.55	13.85	3
2,4,6 Trifluoroacetanilide*	30.15	30.25	3
P. fluoroacetanilide*	12.40	12.50	3

* Fluoride in aqueous solution after decomposition by oxygen flask combustion.

Results

Spectral Characteristics

Figure 1 shows the absorption spectra of AABS_N in solutions of different pH values (pH = 1, 4, 7, 10 & 13). Figure 2 shows spectra of AABS_N, AABS_N/Zr, AABS_N/Zr/F at pH = 1. The appearance of a new peak at 605 nm (2C & 2E) implies that the fluoride ion reacts with the AABS_N/Zr chelate forming a ternary complex, thus eliminating the alternative possibility of dye displacement from the metal chelate.

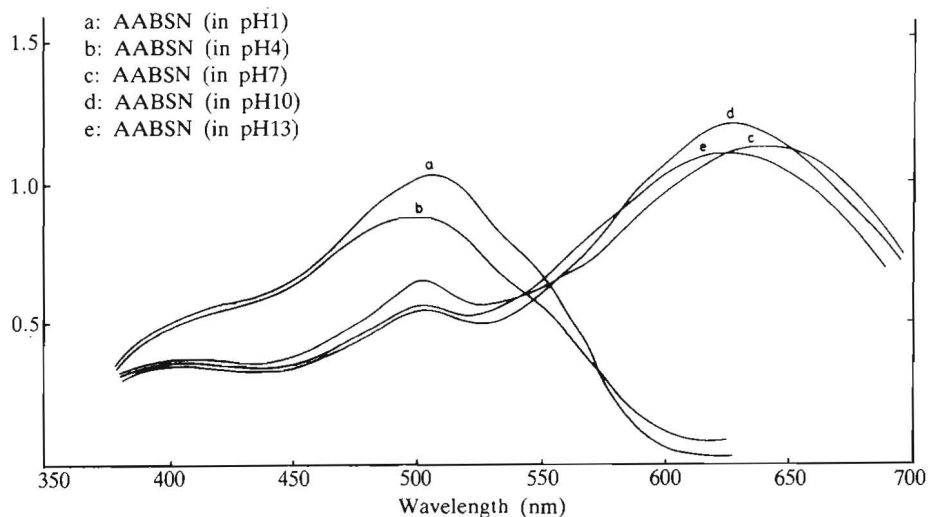


Fig. 1. Absorption curves of AABS_N.

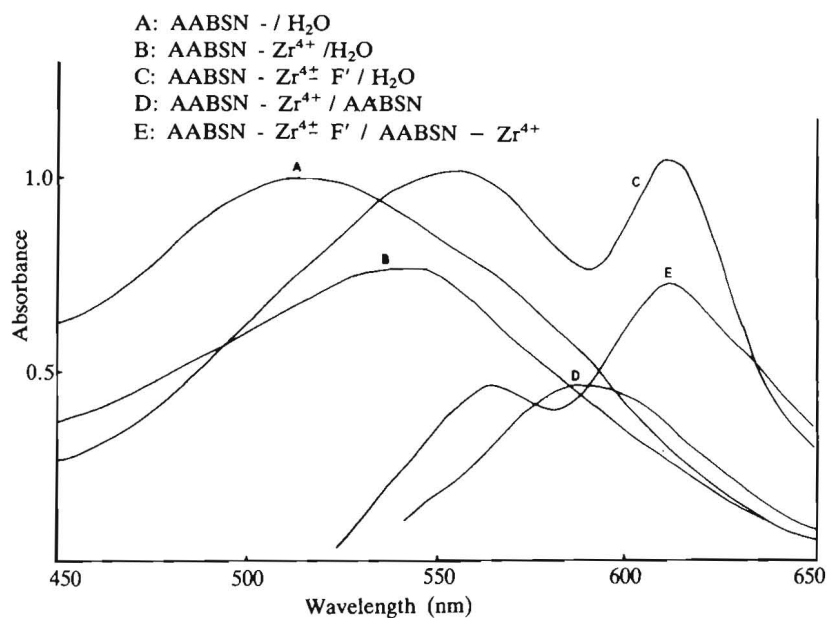


Fig. 2. Absorption spectra of AABS_N-Zr-F.

It has been noticed that the absorbance at 605 nm increases with time up to a constant value, thus all measurements were taken at 605 nm after 5 hr (Table 2).

Table 2. Effect of time on absorbance of complex at 605 nm.

Time (hr)	Absorbance at 605 nm
0.16	0.60
0.50	0.80
1.00	1.00
2.00	1.10
4.00	1.26
6.00	1.26

Effect of pH

Within the pH range studied, the effective pH for the formation of the AABS_N/Zr/F complex has been found to be 1.5. Below pH = (4M, 2M & 1M HCl) a large decrease in the absorbance is observed; at pH = 4 the peak is shifted to 545 nm.

Stoichiometry

The stoichiometric ratio of the AABS_N/Zr complex was determined by Jobs method of continuous variations and the mole ratio method at the same pH(1) for ternary complex formation (Fig. 3 and 4). From both figures, it is clear that AABS_N forms an AABS_N/Zr = 1:1 complex as well as a 2:1 complex. It was observed that a precipitate formed from the 1:1 complex but not from the 2:1 complex.

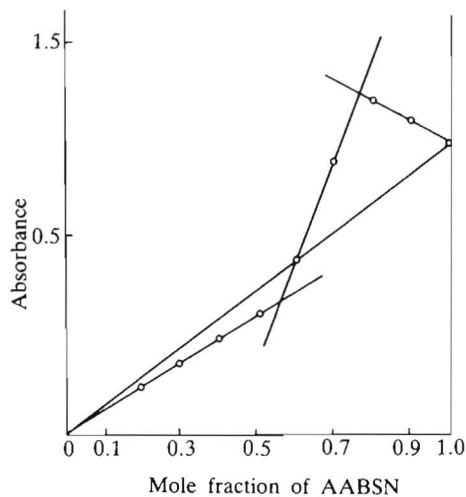


Fig. 3. Jobs plot of AABS_N-Zr.

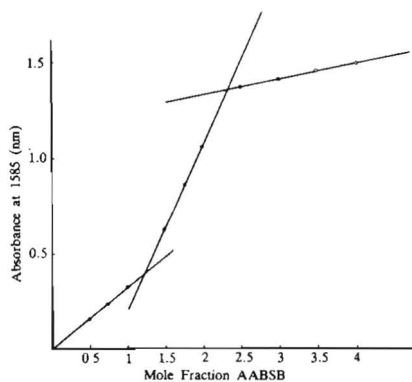


Fig. 4. Mole ratio method plot of AABS_N-Zr.

Figure 5 shows the Jobs plot between the 2:1 AABS_N/Zr complex and the fluoride ion, indicating that the overall complex species is of 2:1:1 type, *i.e.* (AABS_N)₂ZrF.

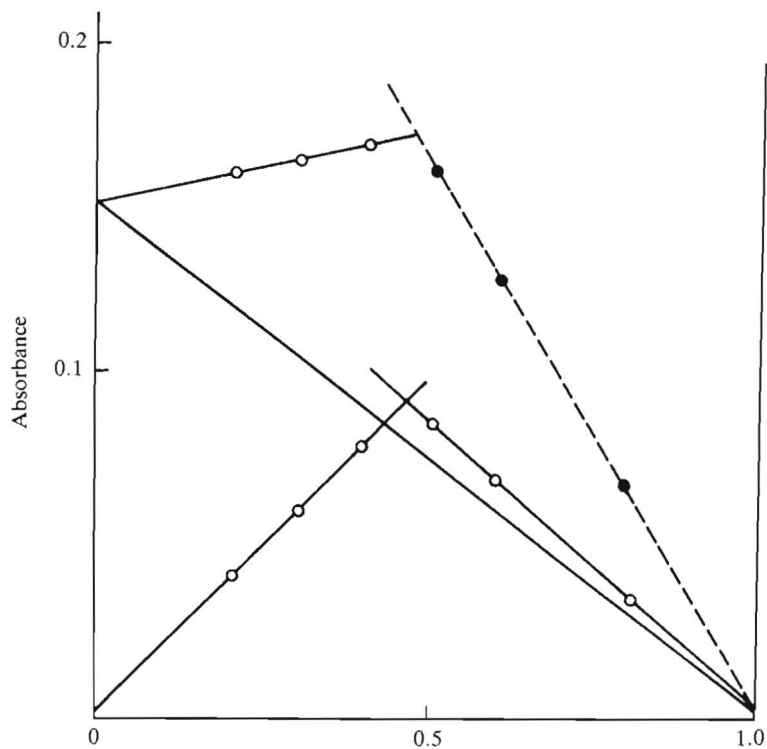


Fig. 5. Jobs plot of AABS_N-Zr.F.

Interference studies

The influence of up to 50-fold molar excess of a selection of 10 other anions likely to interfere by forming complexes or precipitates with zirconium was examined as were the effects of 10 cations likely to form preferential complexes with AABSN or fluoride ion. The results of this study are summarized in Table 3.

Table 3. Interference of various ions in molar excess over 0.4 ppm fluoride ion.

Ions	Results
Arsenate	Interferes at 2 fold excess
Phosphate	Interferes at 2 fold excess
Citrate	Interferes at 2 fold excess
Sulphate	No interference up to 20 fold excess
Cyanide	No interference
Cyanate	No interference
Thiocyanate	No interference
Iodide	No interference
Bromide	No interference
Nitrate	No interference
Th ⁴⁺	Interferes at 1 fold
La ³⁺	Interferes at 1 fold
Cu ²⁺	Interferes at 5 fold excess
Co ²⁺	Interferes at 5 fold excess
Al ³⁺	Interferes at 5 fold excess
Be ²⁺	No interference up to 10 fold excess
Cd ²⁺	No interference up to 10 fold excess
Ca ²⁺	No interference up to 10 fold excess
Ba ²⁺	No interference up to 10 fold excess
Ni ²⁺	No interference up to 10 fold excess
Fe ³⁺	Interferes at 2 fold excess

Discussion

Figure 6 shows the most probable ionisation pattern of AABSN. It is logical to assume that the proton attached to the central phenolic oxygen will behave differently from the other two, and that those latter will behave in an identical fashion because of the symmetry of the molecule. The central phenolic group will ionise first, since the other groups attached to naphthyl residues will be less acidic and additionally will be hydrogen-bonded to the azo group in AABSN. Thus, these two protons will be retained until a much higher pH than the first one. The pH spectra of AABSN in Fig. 1 show two absorption bands, pH 1-4 at 510 nm and pH 7-13 at 610 nm, thus substantiating this hypothesis.

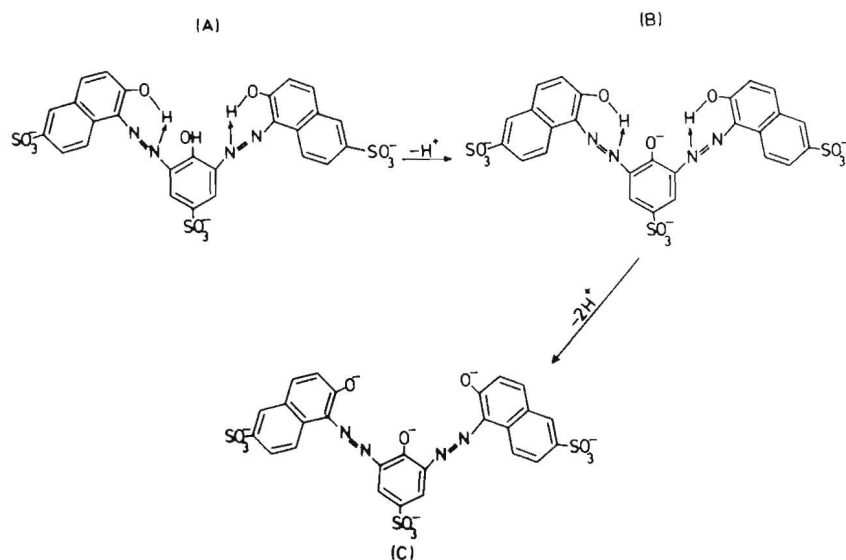


Fig. 6. Ionization pattern for AABSNa vs pH.

Although the stoichiometric study proved the existence of 2:1 AABSNa-Zr and 2:1:1 AABSNa-Zr-F complexes, the interpretation of the stereochemistry of the formulations (Fig. 7) is difficult and such structures shed no light on the mechanism of a possible colour change due to the introduction of the fluoride ion to the AABSNa-Zr chelate.

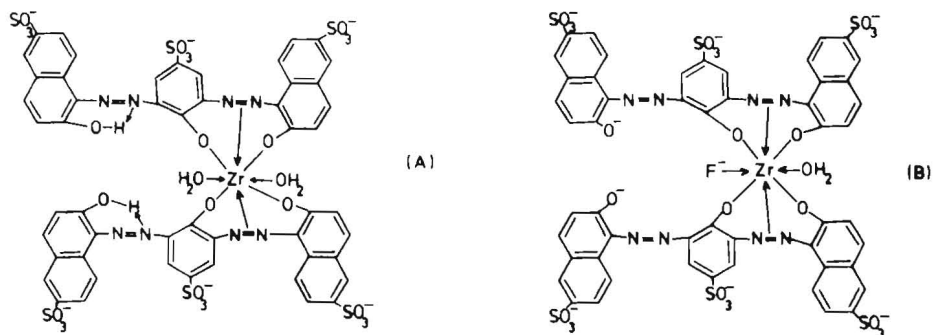


Fig. 7. Suggested structures for
(A) AABSNa-Zr (2/1) (B) AABSNa-Zr-F (2/1/1).

The 1:1 and 1:1:1 configurations proposed in Fig. 8 are based on presence of the 40% Na_2SO_4 which does not upset the reactions in any way. At $\text{pH} = 1$, the AABS molecule can be assumed to be fully protonated (Fig. 8A). Introduction of the Zr^{4+} ion will displace the central phenolic proton (Fig. 8B) but not the other two more strongly retained protons. It is highly probable, at this stage, that the zirconium ion will develop coordinate bonds with the two azo groups. The orange red colour of the Zr chelate does not match exactly the red colour of the monoionized metal-free AABS molecule as might otherwise be expected, because the resonance pathway in the naphthyl azo parts of the molecule has been diminished by breaking of the azo-phenolic hydrogen link; in Fig. 8B the coordinated H_2O molecules on the Zr ion have been omitted in the interests of clarity.

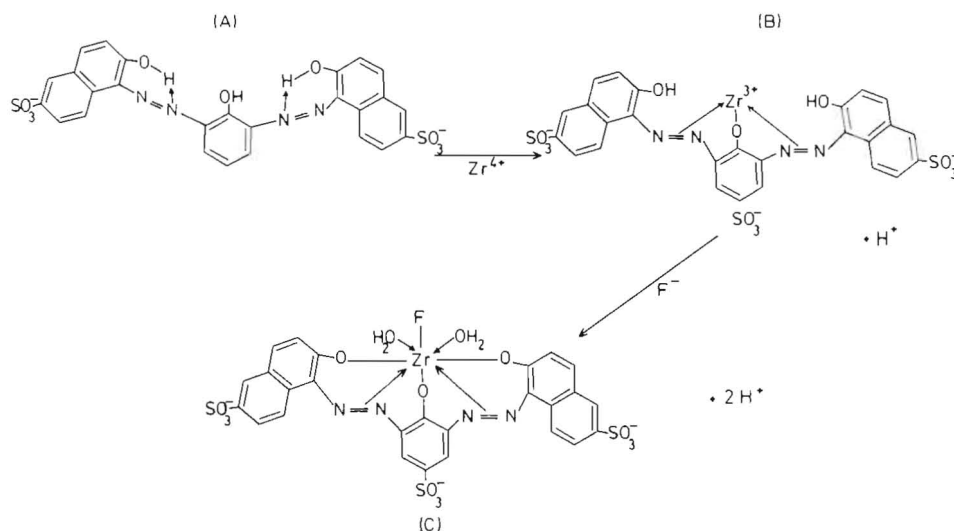


Fig. 8. Suggested chromogenic mechanism for the AABS-Zr-F system.

Entry of the strongly electrophilic fluoride ion into the AABS-Zr chelate (Fig. 8C) results in withdrawal of electrons from the organic ligand *via* the Zr-O bond which according to Pauling (1967) has a partial double bond characteristic. Consequently, the deficiency is transmitted through the conjugated bond system of the AABS chromophore to the remaining phenolic protons which are then caused to ionize. These will then bond to the Zr ion to produce a neutrally charged 1:1:1 AABS-Zr-F complex. The effect of the ionization of the remaining two protons of the chromophore is to produce on absorption change in the AABS-Zr-F complex which closely resembles the colour change of the AABS

on its own at high pH values (Fig. 1 and 6). The bonding of the 3 phenolic oxygen to the Zr, and the bonding of the latter to the azo nitrogens would, however, modify the resonant pathway in the molecule so that the violet colour of the chelate is a modification of the blue colour of the fully ionized AABSN molecule. It is tempting to speculate that the twin peaks of the ternary complex 565 and 605 nm in Fig. 2C might correspond to the involvement of the second and third phenolic oxygens upon introduction of the fluoride ion.

Thus, the electrophilic effect of the fluoride ion which is so clearly shown in the alizarin complexan-zirconium III-fluoride system (West and Leonard 1960) is less well defined in the present system, but the underlying mechanism is clearly the same. In respect of this, therefore, the objective of this search has been successful in that the findings matched the expectation of the theory advanced for the alizarin complexan reagent system.

Conclusions

The method described provides a spectrophotometric method of high sensitivity for the determination of trace amounts of fluoride in aqueous solution down to 0.05 ppm. Of the common anions, phosphate, arsenate and citrate interfere seriously at two fold excess. Very few cations interfere.

Acknowledgement

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References

- Bellack, E. and Schouboe, P.J. (1958) Rapid photometric determination of fluoride in water, *Analyt. Chem.* **30**: 2032-2034.
- Einaga, H. and Iwasaki, I. (1981) Spectrophotometric study of the reaction of zirconium with Chrome Azurols and fluoride, *Talanta* **28**: 889-900.
- Knapp, G. (1970) Catalytic determination of small amounts of fluoride using the zirconium - xylenol orange reaction, *Mikrochim. Acta* **3**: 467-469.
- Megregian, S. (1954) Rapid spectrophotometric determination of fluoride with zirconium - Erichrome cyanine R, *Analyt. Chem.* **26**: 1161-1166.
- Pauling, L. (1967) *The Chemical Bond*, Oxford University Press, pp. 171-173.
- Schoniger, W. (1955) Rapid microanalytical determination of halogen in organic compounds, *Mikrochim. Acta* 123-129.
- West, T.S. and Leonard, M.A. (1960) Chelating reactions of alizarin complexan with metal cations in aqueous media, *J. chem. Soc.*: 4477-4486.
- West, T.S. and Cabello-Tomas, M.L. (1969) Determination of fluoride by catalysis of the zirconium - xylenol orange reaction, *Talanta* **16**: 781-788.
- West, T.S. and Har, T.L. (1971) Spectrofluorimetric determination of traces of fluoride ion by ternary complex formation with zirconium and Calcein Blue, *Analyt. Chem.* **43**: 136-139.

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القياس الطيفي لكميات صغيرة من
أيون الفلوريد بواسطة تكوينه للمعقد
الثلاثي
مع الزركنيوم وحمض الأليزارين
الأسود س . ن .

سلامة بطرس سلامة و توم س . وست

قسم الكيمياء - جامعة الخرطوم - الخرطوم - السودان

أمكن حساب كميات صغيرة من أيون الفلوريد
(١,٠ - ٠,٤ ميكروجرام) في حدود خطأ لا يتجاوز ٢٪
بالقياس الطيفي للمعقد الثلاثي المتكون من صبغة حمض
الأليزارين الأسود س . ن وأيونات الزركنيوم رباعية التكافؤ
وأيونات الفلوريد. ويتميز بذروة امتصاص عند موجة طولها
٦٠٥ نانومتر وامتصاصية مولارية تعادل $٣,٢ \times ١٠^٤$ لتر /
مول^{-١} سم^{-١}.