

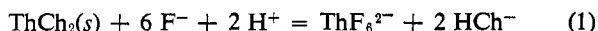
Reaction of Thorium Chloranilate with Fluoride

C. David West,¹ Ronald L. Birke,² and David N. Hume

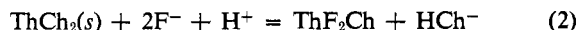
Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Mass. 02139

The reaction between thorium chloranilate and fluoride ions in aqueous pH 4.7 buffer under analytical conditions yields one chloranilate anion in solution for each two fluoride ions, and thorium difluorochloranilate as a solid phase. In 1:1 methyl Cellosolve-water medium, the same reaction takes place but the colored thorium difluorochloranilate is soluble, enhancing the sensitivity. Larger amounts of fluoride lead to the formation of insoluble thorium fluoride.

THE THORIUM CHLORANILATE METHOD, introduced by Hensley and Barney (1) for the colorimetric determination of fluoride, has been found by many workers to be both sensitive and reliable over a large range of fluoride concentrations. Incidental to their description of the method, Hensley and Barney suggested that the reaction taking place in buffered aqueous solution was



and in buffered aqueous methyl Cellosolve



where the complex ThF_2Ch was assumed to be soluble. Because neither the published values for the stability constants of thorium fluoride complexes (2, 3) nor the dissociation constants of chloranilic acid (4, 5) were consistent with these reactions, the present investigation was undertaken.

EXPERIMENTAL

Thorium Chloranilate and Fluoride Reaction Procedure. Solid thorium chloranilate (ThCh_2), Fisher Scientific Co. Reagent Grade, was reacted with fluoride ion in various solvent ratios of methyl Cellosolve (ethylene glycol monomethyl ether) to water. A weighed amount which had been washed with H_2O and then acetone and dried overnight at 105°C and 30 mm in a vacuum oven was added to 100-ml volumetric flask with 10 ml of pH 4.7 acetate buffer. The desired volumes of methyl Cellosolve and fluoride solution, made determinately with reagent grade sodium fluoride, were added to give the desired solvent ratio and fluoride-to-thorium chloranilate mole ratio. The small volume error due to the solid reagent was neglected in making up to volume with deionized distilled water. The mixed solvent solutions were stirred at room temperature with a Teflon-covered magnetic stirring bar for 6 hours and the aqueous solutions for 10 to 24 hours. According to Hensley and Barney (1), equilibrium is reached in 2 hours in the first instance and 6 hours in the second. After equilibration, the solutions were filtered through an ultrafine glass frit to remove suspended matter.

¹ Present address, Occidental College, Los Angeles, Calif. 90041

² Present address, Department of Chemistry, Harvard University, Cambridge, Mass. 02138

- (1) A. L. Hensley and J. E. Barney II, *ANAL. CHEM.*, **32**, 828 (1960).
- (2) H. W. Dodgen and G. K. Rollefson, *J. Am. Chem. Soc.*, **71**, 2600 (1949).
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- (5) P. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56**, 225 (1952).

In order to determine the products formed under analytical conditions 0.2 gram or more of reagent was mixed with buffered solutions $10^{-5}M$ to $10^{-3}M$ in fluoride having ratios of 1:1, 1:3, and 0:1 methyl Cellosolve to water. The same procedure without the addition of fluoride was followed in determining the solubility of thorium chloranilate and in preparing blanks. At very low fluoride concentrations, an alternative technique using all-polyethylene equipment until after the equilibration step was employed. Ultraviolet and visible absorption spectra were obtained with Cary Model 11 or Model 14 recording spectrophotometers. A Beckman DU spectrophotometer was used for some of the individual absorbance measurements. Matched 1-cm quartz cells were used except for part of the UV calibration curve where 0.1-cm cells were found necessary. All spectra were measured against reagent blanks.

X-ray powder diffraction patterns were obtained on dried samples of the solid reaction products obtained at various thorium chloranilate-to-fluoride ratios with the General Electric Model XRD-5 and XRD-3 spectrometers using copper α -radiation with a nickel filter. The samples were mixed with amyl acetate and collodion in preparing the slides.

Radioactive thorium chloranilate was prepared using ^{234}Th separated from uranyl nitrate by the procedure of Dyrssen (6). The active thorium nitrate was added very slowly and with vigorous stirring to the stoichiometric amount of chloranilic acid solution, and an 85% yield of thorium chloranilate obtained. This material was used for the determination of thorium in solution under various conditions. Radioactivity was measured by counting liquid samples in weighing cups covered by a lacquer film (7) using a thin-windowed Geiger Müller tube and a conventional scaling circuit. Elemental microanalysis of Fisher Certified Grade thorium chloranilate and the radioactive preparation were in good agreement, although both indicated the presence of about 6 moles of water per mole of thorium chloranilate. The equivalent weight of the commercial thorium chloranilate was corrected for the presence of 14.2% water as used.

RESULTS AND DISCUSSION

It was assumed by Hensley and Barney (1) that in the aqueous buffer medium, the soluble product of the thorium chloranilate-fluoride reaction was the singly charged anion $\text{HC}_6\text{Cl}_2\text{O}_4^-$. From the published values of pK_1 and pK_2 of chloranilic acid (4, 5) it is evident, however, that at pH 4.7, at least 96% will be in the form of the dianion. The spectra of the dianion, both visible and the ultraviolet, were found to be unchanged on going from water to methyl Cellosolve-water mixtures of composition 1:9, 1:3, and 1:1, with pH 4.7 buffer present. The molar absorptivities were determined to be 2.48×10^4 at 330 μ and 202 at 530 μ .

The solubility of thorium chloranilate is small and, in the visible region where the molar absorptivity is low, makes a negligible contribution to the total absorbance. A saturated solution has no visible color in any but the most concentrated methyl Cellosolve mixtures employed. In the ultraviolet region the absorbance is not negligible as shown in Figure 1. The apparent solubility of thorium chloranilate in pH 4.7

(6) D. Dyrssen, *Svensk Kem. Tidskrift*, **62**, 153 (1950).

(7) A. J. Freedman and D. N. Hume, *Science*, **112**, 461 (1950).

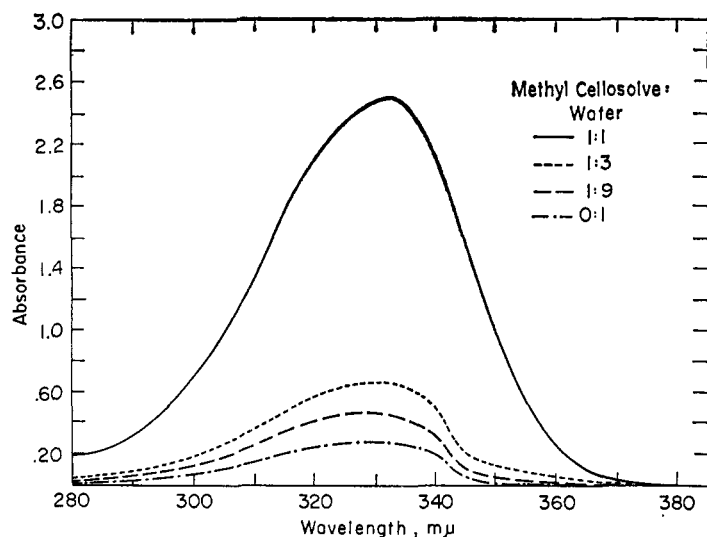


Figure 1. Absorption spectra of pH 4.7 acetate buffer saturated with thorium chloranilate, as a function of methyl Cellosolve content

buffer at methyl Cellosolve–water ratios of 0:1, 1:9, 1:3, and 1:1 was found to be $6.0, 9.5, 13$, and $50 \times 10^{-6}M$ assuming two chloranilate ions released per mole dissolved. Measurement of radioactivity in a saturated 1:1 methyl Cellosolve–water solution of thorium chloranilate made from ^{234}Th indicated a solubility of about $120 \times 10^{-6}M$, with the thorium activity in saturated solutions containing smaller proportions of methyl Cellosolve being too low to measure.

The stoichiometry of Reactions 1 and 2 was arrived at by Hensley and Barney solely on the basis of a comparison of the absorbance of solutions of known fluoride concentration which had been treated with excess thorium chloranilate with the absorbance of solutions of known chloranilate concentration. From measurements on very dilute aqueous solutions at $330\text{ m}\mu$ they concluded that one chloranilate ion, or its equivalent, was liberated by reaction of three fluoride ions, leading to the stoichiometry expressed by Equation 1. Our observations, using somewhat less dilute aqueous solutions at $530\text{ m}\mu$, show the release of one chloranilate ion by two fluoride ions (Table I). The measured absorbance of 1.00 mM solutions of standard sodium fluoride equilibrated with excess thorium chloranilate in aqueous medium checked within 1% of that calculated for 0.500 mM chloranilate. Indeed, the slope of the aqueous calibration curve at $530\text{ m}\mu$ published by Hensley and Barney indicates a stoichiometry nearer 2:1 than 3:1 fluoride to chloranilate. On checking the calibration curve at $330\text{ m}\mu$ for very low concentrations of fluoride using the aqueous buffer systems, it was found that above $3 \times 10^{-4}M$ the curve was linear with a slope of 2.01 fluoride per chloranilate, but below $3 \times 10^{-4}M$ there was considerable curvature leading to apparent ratios of fluoride to chloranilate even greater than 3:1 (Figure 5). The same phenomenon of deviation from linearity at low concentrations with apparent ratios of chloranilate to anion higher than theoretical and a positive intercept of the extrapolated linear calibration curve on the concentration axis was observed for the barium chloranilate–sulfate system by Agterdenbos and Martinus (8). These workers showed that the phenomenon was due to the effective buffering of the chloranilate concentration

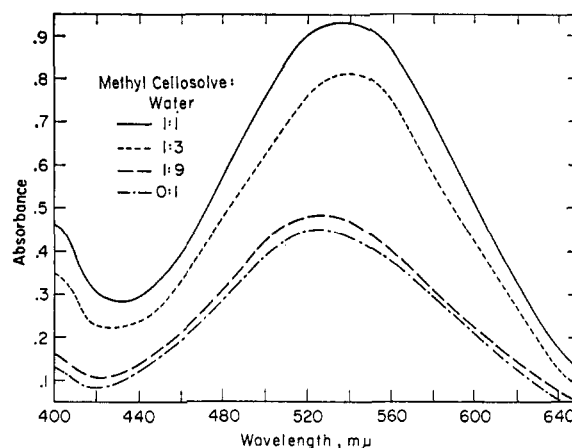


Figure 2. Absorption spectra of soluble thorium chloranilate–fluoride reaction product as a function of methyl Cellosolve content

Concentration of added fluoride $5.26 \times 10^{-3}M$

by dissolved barium chloranilate and an analogous process is most likely to be the explanation here. This, however, is not ordinarily a source of analytical error inasmuch as methyl Cellosolve–water mixtures are invariably used for the determination of very low fluoride concentrations.

Also given in Table I are the results of equilibrations done in buffered mixtures of methyl Cellosolve and water. In agreement with Hensley and Barney it was observed that methyl Cellosolve changed neither the wavelength nor the absorptivity of the chloranilate maximum, but the wavelength of maximum absorbance was shifted slightly to longer wavelengths and the apparent absorptivity increased for the reaction product as the methyl Cellosolve content was increased (Figure 2). It was further found that in a 1:1 methyl Cellosolve–water system addition of 2 moles of fluoride per mole of thorium chloranilate gave an absorbance nearly 50% greater than would have been expected if all the thorium chloranilate had been converted to free, soluble chloranilate. Further addition of fluoride did not increase the absorbance but, on the contrary, decreased it until a total of approximately 4 moles of fluoride per mole of thorium had been added, after which it remained constant. This was in harmony with the hypothesis that a different reaction product is formed in methyl Cellosolve solutions and further experiments were devised to determine the nature of the reactions in both media.

Table I. Apparent Molar Absorptivities of the Reaction Product^a

Solvent ratio MeCel: H ₂ O	UV peak		Visible peak	
	λ_{max}	ϵ^b	λ_{max}	ϵ^b
0:1	330 mμ	8.0×10^3	530 mμ	99
1:3	332 mμ	19.0×10^3	535 mμ	150
1:1	332 mμ	23.0×10^3	535 mμ	310

^a Conditions: 100 ml of solution containing 10 ml of pH 4.7 acetate buffer and 0.2 gram of thorium chloranilate. Fluoride concentration $5.26 \times 10^{-3}M$ in UV experiments, $1.00 \times 10^{-3}M$ in visible.

^b Absorptivity per mole of fluoride.

(8) J. Agterdenbos and N. Martinus, *Talanta*, **11**, 875 (1964).

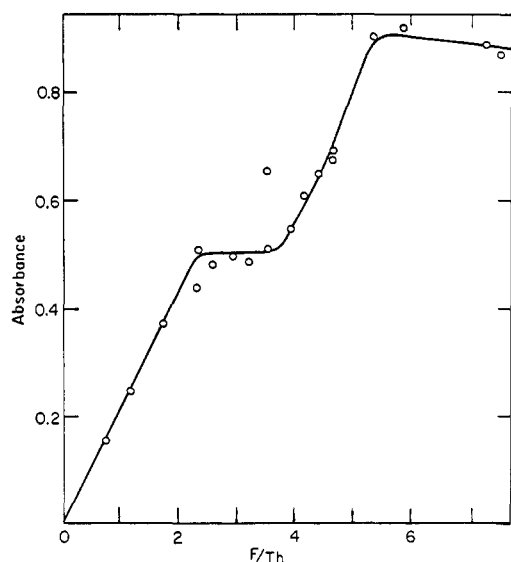


Figure 3. Absorbance at 530 $m\mu$ of aqueous pH 4.7 acetate buffer solutions containing various amounts of fluoride, after equilibration with 0.267 mmole of thorium chloranilate

Abscissa is the ratio of moles of fluoride added per mole of thorium chloranilate

A plot of the maximum absorbance at 530 $m\mu$ vs. the mole ratio of fluoride to thorium chloranilate initially present was obtained to investigate the reaction in buffered aqueous solutions (Figure 3). X-ray powder diffraction patterns were taken on the residues and, for comparison, on the Fisher thorium chloranilate used as starting material. Three different solid phases were distinguishable in the various residues (Figure 4). The pattern characteristic of a new solid phase began to appear along with that of thorium chloranilate as the fluoride-to-thorium mole ratio was increased, and became predominant by a mole ratio of 1.5:1. At a mole ratio of 2:1 only the lines characteristic of this phase were visible. The lines of a second new phase became visible at about 3.5:1, and by 4.5:1 had supplanted all others. The pattern of this phase was characteristic of all residues at high mole ratios. Elemental analysis of the dried residue showed carbon-to-thorium atomic ratio of about 5.6:1 in the silver gray material from an equilibration at a 2.5:1 fluoride-to-thorium chloranilate mixture. A residue from a 10:1 fluoride-to-thorium chloranilate mixture, on the other hand, was faintly pink, had only traces of carbon present, and having the proper weight, was assumed to be thorium fluoride.

Table II. Demonstration of Excess Fluoride in Solution at F:Th Ratios Between 2 and 4

Mole ratio F/Th	Absorbance ^a	Absorbance ^b	Predicted ^c
2.33	0.442	0.498	0.506
2.94	0.500	0.632	0.630
3.50	0.658	0.772	0.758

^a Measured after equilibration in the usual manner.

^b Filtered solution re-equilibrated with additional ThCh_2 and corrected for dilution.

^c Calculated on basis of complete reaction of added fluoride to give 0.5 mole of chloranilate per fluoride.

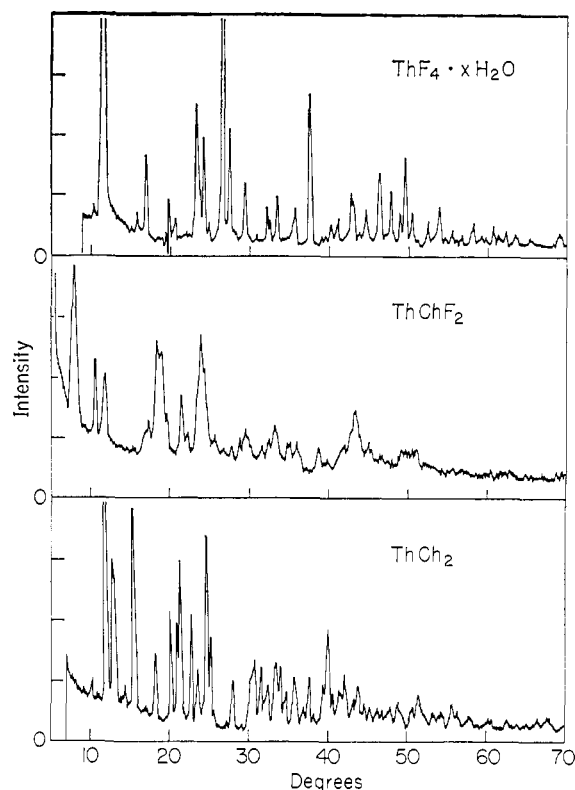


Figure 4. X-ray diffraction patterns of hydrated thorium fluoride formed by reaction of thorium chloranilate with excess fluoride, thorium fluorochloranilate from reaction of two fluorides per thorium chloranilate, and of thorium chloranilate: intensity vs. 2θ

The absorption spectrum of the equilibrated solutions in the first part of Figure 3 was identical with that of chloranilic acid in the same buffer, and on the basis of the measured absorption coefficient of the chloranilate anion, it was evident that 1 mole of chloranilate was being released into the solution for each 2 moles of fluoride added. The break in the curve at a mole ratio about 2, together with the X-ray evidence, the elemental analysis, and the change in color of the residue indicates complete conversion of the thorium chloranilate to a new phase having the composition ThChF_2 at this point. The stability of the X-ray pattern between mole ratios of 2.5 and 3.5 coincident with the plateau in Figure 3 raised the question as to whether the fluoride was reacting or remaining in solution. To answer this, mixtures were made to contain 2.3, 2.9, and 3.5 moles of fluoride per mole of reagent according to the standard procedure, and filtered after 12 hours of equilibration. Fresh thorium chloranilate in excess was then added to the filtrates, and after 12 hours equilibration, they were filtered again and the absorbances measured. The results in Table II show that considerable fluoride in excess of the 2:1 ratio had remained in solution in the original equilibration. Further reaction of ThF_2Ch with fluoride in very dilute solution is evidently slow and a significant excess is needed to push the reaction all the way to thorium fluoride at an appreciable rate. Points on the initial part of the curve, corresponding to the range which would be used analytically, could be reproduced to about 1%. In the range of above two fluorides per thorium, the reproducibility was about 5%, as might be anticipated when the extent of reaction was limited by a slow final step. Occasionally, equilibrations at 3.5 to 1 resulted in the anomalous appearance

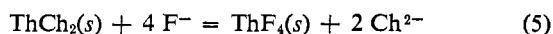
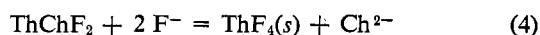
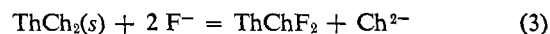
of larger amounts of chloranilate in solution without the concurrent appearance of thorium fluoride lines in the X-ray pattern of the residue. This was not investigated further.

Attempts were made to match the X-ray diffraction pattern of the reaction product formed in the presence of excess fluoride with published patterns for thorium fluoride hydrates. D'Eye and Booth (9) had reported considerable difficulty in getting distinct patterns for thorium fluoride precipitates, many of their products being X-ray amorphous. They gave $\sin^2 \theta$ values for a product $\text{ThF}_4 \cdot 2.5\text{--}3.0 \text{ H}_2\text{O}$, observing that the lines were too weak for unambiguous indexing, and for a second product, $\text{ThF}_4 \cdot 0.8\text{--}1.6 \text{ H}_2\text{O}$ for which the patterns were somewhat stronger. In the present work, a precipitate of the 2.5–3.0 hydrate was prepared by the method of D'Eye and Booth, with reasonably sharp peaks and a diffraction pattern similar to that previously reported, but only after several weeks of digestion. Attempts to prepare the monohydrate always resulted in material which was X-ray amorphous. In contrast, the ultimate reaction product of thorium chloranilate and excess fluoride gave a very sharp X-ray pattern which did not match any previously reported (Figure 4). Analysis indicated the presence of between 1 and 2 moles of water per thorium. Whether the more orderly crystal lattice obtained through the reaction of thorium chloranilate is due to a templating effect of the ThF_2Ch lattice or simply to the slow crystallization resulting from low relative supersaturation cannot be decided from the present data.

If the high absorbances obtained in mixtures of methyl Cellosolve and water are to be explained by the presence of a soluble thorium chloranilate fluoride complex, then significant amounts of thorium must be present in the solutions. To determine if this were the case, the thorium chloranilate prepared with radioactive thorium was used in equilibrations both in aqueous buffer and in mixtures with methyl Cellosolve (Table III). It is seen that within the considerable experimental uncertainty of the radioactive solubility measurements, (about $\pm 5 \times 10^{-6} M$ thorium) nearly 0.5 mole of thorium are dissolved per mole of fluoride added in 1:1 methyl Cellosolve medium, while in aqueous medium the ratio is about 40-fold smaller.

CONCLUSIONS

Evidence has been given that the Reactions 3, 4, and their combination 5 occur in both water and aqueous methyl Cellosolve mixtures



and offer an explanation of the observed phenomena in the thorium chloranilate method for determining fluoride. The neutral complex, ThChF_2 , is quite insoluble in water but becomes increasingly soluble as the ratio of methyl Cellosolve to water increases. The increased sensitivity found in aqueous methyl Cellosolve is due, in part, to the solubility of the neutral species and in part to its increased absorptivity compared to the chloranilate ion. The experimental data show no

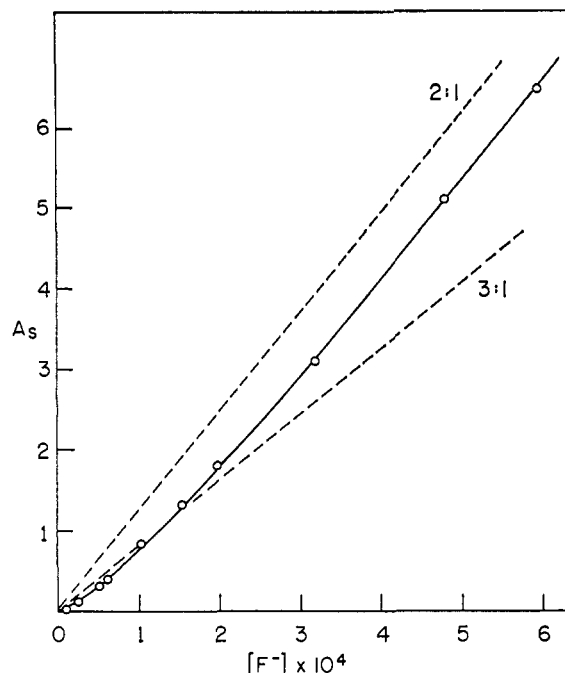


Figure 5. Calibration curve at 330 $m\mu$ in aqueous medium

Cary 14 spectrophotometer and overnight equilibration. 1-cm cells used in lower region, 1-mm cells above $2 \times 10^{-4} M$ fluoride and corrected to 1-cm path length. Dotted lines show theoretical slopes based on assumed 2:1 and 3:1 F/Th stoichiometry releasing chloranilate anion

evidence that the ThF_6^{2-} species, previously proposed to give a reaction with 3:1 stoichiometry in aqueous solution, exists.

From the standpoint of practical analytical application, the results of the present work confirm the findings of previous workers that the method is convenient, sensitive, and reliable. It should be noted, however, that at very low fluoride concentrations where the ultraviolet peak must be used, there is danger of nonlinearity, which is particularly striking in the purely aqueous solvent. The reagent blank in higher methyl Cellosolve concentrations also becomes quite large in the ultraviolet and may become a source of error with samples low in fluoride. The procedure of Hensley and Barney does not call for sufficient thorium chloranilate for fluoride concentrations above 3 mg/100 ml if a safe excess is to be maintained, and it is recommended that

Table III. Thorium Concentrations after Equilibration
Th: F Ratios from 1.27 to 5.0

Methyl Cellosolve-water ratio	Fluoride added, M	Thorium concentration, M	Moles Th dissolved per mole F
1:1	2.1×10^{-3}	8.62×10^{-4}	0.41
1:1	1.05×10^{-3}	4.74×10^{-4}	0.45
1:1	5.3×10^{-4}	2.15×10^{-4}	0.41
1:3	2.1×10^{-3}	2.0×10^{-4}	0.10
1:3	1.05×10^{-3}	1.23×10^{-4}	0.18
1:3	5.3×10^{-4}	6.2×10^{-5}	0.18
0:1	2.1×10^{-3}	1.8×10^{-5}	0.0085
0:1	1.05×10^{-3}	1.3×10^{-5}	0.013
0:1	5.3×10^{-4}	9×10^{-6}	0.018

(9) R. W. M. D'Eye and G. W. Booth, *J. Inorg. Nuclear Chem.*, **1**, 326 (1955).

0.25 gram be used if the range is to be extended to 10 mg/100 ml. When using the aqueous procedure, difficulty may be experienced in filtering out the very finely divided thorium fluorochloranilate which is formed. High retention filter paper was sometimes found to be ineffective and filtration through an ultrafine-porosity-glass frit is strongly recommended. The rate of equilibration in the absence of methyl Cellosolve tends to be inconveniently slow, especially for higher fluoride concentrations, and overnight equilibration with effective stirring is a necessity if good precision is to be obtained.

Finally, it is suggested that Equation 4 in water offers a convenient method of obtaining a crystalline form of hydrated

thorium fluoride not previously observed. Although the number of moles of water of hydration is not definite, the data suggest that it is between one and two.

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Determination of Fluoride by Atomic Absorption Spectrometry

A. M. Bond and T. A. O'Donnell

Department of Inorganic Chemistry, University of Melbourne, Parkville 3052, Victoria, Australia

Fluoride ion depresses the absorption of magnesium in the air-coal gas flame, the change in absorbance of the magnesium resonance line at 2852 Å being proportional to the fluoride concentration over the range 0.2–20 µg/ml (10^{-5} – 10^{-3} M). In the absence of interfering ions, principally sulfate and phosphate, the effect can be used to determine fluoride ion in this concentration range. An alternative, though somewhat less sensitive, technique is based on the enhancement of zirconium absorption by fluoride ion in the nitrous oxide-acetylene flame; this allows the determination, with a high degree of freedom from interference, of fluoride ion over the range 5–200 µg/ml (2.5×10^{-4} – 10^{-2} M). In the presence of phosphate, which interferes with the zirconium method, a similar enhancement of titanium absorption can be used for fluoride determinations in the range 40–400 µg/ml (2×10^{-3} – 2×10^{-2} M). These atomic absorption methods for fluoride determinations have been found to be considerably more rapid than more classical methods and in many cases can be used directly without prior separation of fluoride. Their application has been demonstrated in the analysis of a wide range of inorganic fluorides.

THE MANY SHORTCOMINGS of existing methods for fluoride analysis have been discussed by O'Donnell and Stewart (1). Frequently, to obtain satisfactory results, it is necessary to use tedious and complicated separation procedures, such as the Willard-Winter distillation technique. However, traces of fluoride have a marked depressing effect on the absorbance of magnesium in the air-coal gas flame (2) and an enhancing effect on that of zirconium and titanium in the nitrous oxide-acetylene flame (3). This suggested the possibility of using an indirect atomic absorption technique for rapid and reliable determination of low concentrations of fluoride in aqueous solution.

EXPERIMENTAL

The atomic absorption measurements were carried out using Techtron AA-100 and AA-4 spectrophotometers.

Appropriate Techtron burners were used to provide an air-coal gas flame for the magnesium measurements and nitrous oxide-acetylene flames for zirconium and titanium.

All solid reagents were Reagent Grade. Hydrofluoric acid (Baker Analyzed) was used for some determinations.

DETERMINATION OF FLUORIDE BY DEPRESSION OF MAGNESIUM ABSORBANCE

Magnesium is partially atomized in low-temperature flames such as air-coal gas or air-propane (4); but the concentration of atoms in the flame is very sensitive to the presence of other cations and anions (5, 6), particularly those such as aluminum, phosphate, silicate, and sulfate. These combine with magnesium to form refractory compounds which are not atomized at the temperature of such flames.

Fluoride ion was also found to have a depressing effect on magnesium absorption, and on that of several other metals including calcium, strontium, barium, lead, and iron. However, because of the very high sensitivity of the atomic absorption method for magnesium, the depressing effect of a given concentration of fluoride is greater for magnesium than for any of the other metals. Figure 1 shows the effect of fluoride ion on the absorbance of varying concentrations of magnesium. Except at fluoride concentrations which are very low relative to the magnesium concentration, the absorbance of magnesium falls linearly with addition of fluoride and reaches a constant value at a concentration corresponding roughly to a magnesium-to-fluoride ratio of 1:2. Other authors (7) have found a similar effect for fluoride-containing

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