

## Spectrophotometric Determination of Atmospheric Fluorides

### 1. INTRODUCTION

Fluoride is a special hazard to vegetation where as little as 0.1ppb may affect certain species such as Chinese apricot and some varieties of gladiolus. Although most plants can tolerate many times this concentration and animals are generally unaffected by two or three orders of magnitude higher concentrations than this, it is important that the analytical method used for determining fluorides be capable of great sensitivity and applicable over a wide range of concentrations. A critical problem presented in the determination of atmospheric fluorides is that of sampling. The usual sampling procedures involve trapping the fluoride in an aqueous system whereby not only fluoride but also other pollutants are captured. Although fluoride can co-exist in dilute atmosphere with iron, aluminum, manganese, calcium, magnesium and lead, aqueous solutions of the respective ions react to form insoluble salts and stable complexes. Particularly in the case of the slightly dissociated iron, aluminum and manganese complexes, steps must be taken to isolate the fluoride before final analysis because determinative procedures are incapable of measuring undissolved fluoride.

Many methods have been evolved for the determination of fluoride. The fluoride electrode is excellent for determining fluoride activities in the microgram per milliliter range but is not sufficiently sensitive for air pollution studies except where large volumes of air are being sampled or very high concentrations of fluoride are anticipated. Many spectrophotometric methods have been proposed, most of which are based on the bleaching of a colored species of a chelated metal. The fluoride in such procedures complex the metal responsible for the colored species, thus destroying the color. In 1959, Belcher and Leonard introduced the first reagent for fluoride that produced a color rather than destroying one (11.2). A modification of this sensitive and highly selective reagent (11.2) is utilized together with a unique sampling technique to provide a sensitive, rapid, and specific method for fluoride monitoring (11.4).

A number of approaches have been used to remove interferences or isolate fluoride so that final analytical measurement can be made reliable. Ion exchange has found some use but most monitoral work has relied on distillation. The classic Willard-Winter distillation effectively breaks down stable fluoride compounds and liberates the fluoride from interfering materials. The method is laborious, however, and the use of microdiffusion provides an attractive alternate approach (11.1). The method of dynamic volatilization has advantages of flexibility and rapidity and is described below.

## 2. SCOPE AND FIELD OF APPLICATION

The lanthanide-alizarin complexan-fluoride reaction is the basis for the spectrophotometric determination of atmospheric fluorides. Optimum reaction conditions have been established and the sampling procedure eliminates the interference of diverse ions and molecules that are commonly present in the atmosphere. The method has a sensitivity of  $0.0019\mu\text{g}$  fluoride per sq. cm. and is reproducible within  $\pm 0.003\mu\text{g}$ , per ml at the 95% confidence level for known concentrations of fluoride of  $0.400\mu\text{g}$  per ml. The procedure is uniquely suitable for the determination of actual fluoride concentrations in ambient atmospheres at parts per billion levels. It is well suited for use in mobile laboratories and fixed base monitoring stations.

## 3. PRINCIPLE OF THE METHOD, REACTION, AND SPECIFICITY

The method involves the elimination of interfering species by use of a pre-scrub through hot ( $70^{\circ}\text{C}$ ) sulfuric acid, followed by the trapping of liberated HF in an aqueous system with subsequent spectrophotometric determination with lanthanum-alizarin complexan. The final trapping solution contains sulfamic acid which reacts with any nitrite that might be present, converting it to non-interfering nitrogen gas. All interferences that are likely to be present in the atmosphere are thus eliminated, either by the initial  $\text{H}_2\text{SO}_4$  trap or by the reaction in the final absorbing system.

## 4. REAGENTS AND MATERIALS

### 4.1 *Standard fluoride solution ( $5\mu\text{g}$ per ml)*

Dissolve 0.221 gram of reagent grade NaF in distilled water and dilute to 1 liter. This solution contains  $100\mu\text{g}$  fluoride per ml. Dilute 1 to 20 to obtain the working solution.

### 4.2 *Buffer solution*

Combine 188 grams of anhydrous NaOAc with 336ml of glacial HOAc and dilute to 1 liter with distilled water. When this solution is diluted to 1 to 10 with distilled water, the pH should be 4.3.

### 4.3 *Alizarin complexan ( $1 \times 10^{-3} \text{ M}$ )*

Dissolve 0.385 gram of reagent in a minimum amount of dilute NaOH. Dilute to 1 liter with a buffer solution containing 34ml of glacial HOAc and 18.8 grams of anhydrous NaOAc per liter.

#### 4.4 Lanthanum nitrate-buffer ( $2 \times 10^{-3} M$ )

Dissolve 0.866 grams of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 102 grams of anhydrous NaOAc in 400ml of distilled  $\text{H}_2\text{O}$ . Add 222ml of glacial HOAc and 890 milliequivalents of HCl. Dilute to 1 liter. The pH of this solution, when diluted 1 to 10 and containing acetone to the extent of 25% (v/v) should be 4.1-4.2.

### 5. APPARATUS

5.1 Spectrophotometer – Beckman DU, or equivalent.

5.2 Heating mantel, with powerstat.

5.3 Glass scrubbers – Fritted glass, 30ml.

### 6. SAMPLING

When fluorides are scrubbed from the atmosphere prior to analysis, a number of species containing iron, aluminum, calcium magnesium, and lead are also trapped and thus put into solution along with the isolated fluorides. The resultant formation of insoluble substances such as calcium fluoride, and lead fluoride introduces potential interference and certainly the formation of extremely stable complexes such as the hexafluoroaluminate and the hexafluoroferrate (III) must mask fluorides so that subsequent analytical determination gives values representing fluoride activities after sampling rather than the significant fluoride concentrations of the atmosphere before sampling. The following analytical procedure takes these and other potential interferences into consideration.

The majority of the interferences can be eliminated quite readily while the air sample is being collected. This is accomplished by placing a pre-scrubber containing concentrated sulfuric acid between the sample source and the absorption solution. If the pre-scrubber is heated to approximately  $70^\circ\text{C}$ , the volatile acids will pass over into the absorbing solution leaving any interfering cation in the sulfuric acid. It is assumed that particulates and aerosols are immediately dissolved in the hot acid, thus liberating the  $\text{F}^-$ .

Samples should be collected in a sample train consisting of an inlet tube made of stainless steel or Tygon tubing connected to a 30ml fritted glass bubbler containing approximately 20ml. of concentrated  $\text{H}_2\text{SO}_4$  maintained at  $70^\circ\text{C}$  by an appropriate heating mantel. The scrubbed sample is next led directly into a second fritted glass bubbler containing 30ml of 0.05% sulfamic acid.



## Spectrophotometric Determination of



### 1. INTRODUCTION

Nitric acid and nitrates in air can be measured conveniently by means of the chromotropic acid (9.1) or brucine (9.2) methods. Likewise, mixtures of nitric oxide, nitrous anhydride and nitrogen tetroxide can be converted to equivalent nitrate and estimated as such (9.3). Other methods such as the phenol-disulfonic acid procedure, reduction to nitrite with subsequent measurement by means of a modified Griess reaction or the use of ultra-violet spectrophotometry have been proposed but are not recommended for general use because of lack of specificity or sensitivity or both. The chromotropic acid method is chosen in preference to the brucine procedure because the latter may suffer from interferences due to oxidants, other than nitrate, that may be present in the air.

### 2. SCOPE AND FIELD OF APPLICATION

This is a method for determining trace quantities of nitrate in the air suitable for establishing ambient air quality for spot checks, monitoring, or field surveys. Reliable results can be obtained over the range of 0.5-50 $\mu$ g of nitrate. Interferences due to substances such as nitrite, oxidizing agents, chloride and iron (III) which normally interfere in nitrate determinations have been eliminated.

### 3. PRINCIPLE

The method is based on the reaction of nitrate with chromotropic acid. The absorbance of the resulting yellow solution is proportional to the nitrate concentration. Potential interferences have been eliminated. Addition of excess sodium sulfite removes the interference due to oxidizing agents, and addition of urea eliminates nitrite as nitrogen gas. Chloride is masked by the addition of antimony (III).

### 4. REAGENTS

#### 4.1 Standard nitrate solution

Dissolve 1.371g of reagent grade sodium nitrate in distilled water and dilute to one liter. This gives a nitrate concentration of 1mg/ml. A series of standards can be prepared by suitable dilutions.

#### 4.2 Sulfuric acid

Use analytical reagent grade concentrated acid which is free from nitrate. (Readily checked by adding 1ml reagent to 10ml sulfuric acid. No color should be formed.)

#### 4.3 Purified chromotropic acid

Prepare a saturated solution of the disodium salt of 1,8-dihydroxy-3,6-naphthalene disulfonic acid. Process twice using decolorizing charcoal. Crystallize the reagent from the filtered solution by adding sulfuric acid. Filter; wash several times with ethanol; and dry below 80°C. Prepare a 0.1% solution of the reagent in concentrated sulfuric acid. The reagent solution is colorless and is stable for two weeks.

#### 4.4 Sulfite – urea solution

Dissolve 5g of urea and 4g of reagent grade anhydrous sodium sulfite and dilute to 100ml with distilled water.

#### 4.5 Antimony solution

Heat 0.5g of antimony metal in 80ml of concentrated sulfuric acid until all the metal is dissolved. Cool the solution and add to 20ml of ice water. When kept overnight, if any salt crystallizes, redissolve by heating.

### 5. APPARATUS

#### 5.1 High volume sampler

Spectrophotometer suitable for measurement of absorbance at 410nm and equipped with matched quartz cells.

### 6. SAMPLING

A high volume sampler is used for sample collection. Since nitrates are soluble in water, they can be eluted from the filter paper by repeated washing with a small amount of distilled water. Combine the washings and make up to 100ml with distilled water.

### 7. PROCEDURE

Pipet 2.5ml of each sample or standard solution into dry 10ml volumetric flasks. To each flask add 1 drop of sulfite-urea solution; place the flasks in a

co-pollutants during sampling and if fiber glass filters are used, the acid is partially neutralized by alkaline sites present on the filter surface.

The method chosen for recommendation here is simple, sensitive and rapid. It is based on stoichiometric reactions of dissociated protons and employs the use of an inexpensive ring oven for processing the samples and reaction products (11.8).

## 2. SCOPE AND FIELD OF APPLICATION

The ring oven method for the determination of sulfuric acid aerosol is sensitive, rapid and easy to perform. It is based on the measurement of dissociated protons and by slight alteration in procedure, can be used either for determination of total non-volatile acid ( $H_2SO_4$ ) or for total protons from dissociated acids and from the hydrolysis of salts such as ammonium sulfate, ammonium chloride, and zinc sulfate, which react with moisture to produce protons. The method is readily employed for field studies as well as for determinations made on collected samples and returned to the laboratory.

## 3. PRINCIPLE

This method combines the sampling and determination of sulfuric acid aerosol so that the process is essentially analysis *in situ*. A relatively small sample is collected on quantitative filter paper using a sequential tape sampler or other suitable device that will collect the acid on a spot one inch (or one-half inch) in diameter. The filter itself is then used as the reaction medium for the analytical measurement which is based on the stoichiometric release by acid protons of bromine from a mixture of bromide and bromate. The liberated bromine is reacted with fluorescein to produce eosin, the color of which is measured against standard colors as a direct determination of proton concentration. The measurement steps are performed using a ring oven.

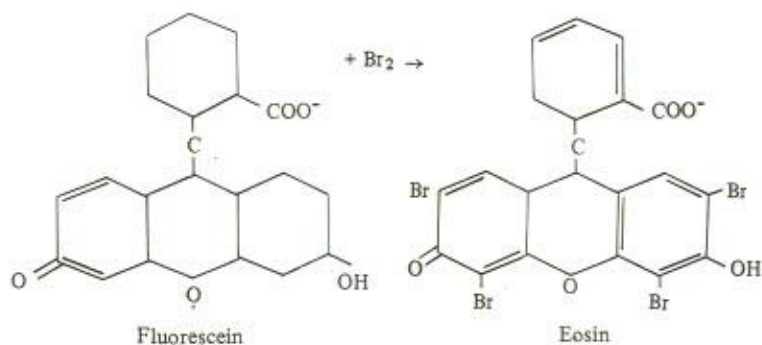
If non-volatile acid ( $H_2SO_4$ ) is to be measured the filter on which the sample has been collected should be heated at 100-105°C for 4 or more hours to eliminate any volatile acids.

## 4. REACTIONS

The determination is based on the stoichiometric release by protons of bromine from a mixture of bromide and bromate as depicted by the following equation:



The liberated bromine is reacted with fluorescein to produce the tetrabromofluorescein (eosin) which has a distinctive orange color.



The intensity of the eosin color is measured against color standards to determine the amount of acid present in the sample.

## 5. REAGENTS AND SOLUTIONS

5.1 Sodium fluorescein – 0.05%; stable for 10 days.

5.2 Potassium bromide – 4.0%.

5.3 Potassium bromate – 4.0%.

5.4 Standard stock sulfuric acid – 0.100 N ( $1\mu\text{l} = 4.9\mu\text{g H}_2\text{SO}_4$ ; dilute as desired to prepare standard working solutions).

## 6. APPARATUS

### 6.1 *Sequential tape sampler*

Bendix Unico Paper Tape Sampler; Research Appliance Company, ASI Automatic Tape Sampler.

### 6.2 *Ring oven with accessories*

Trace oven, Arthur H. Thomas, Co.

### 6.3 *Miscellaneous supplies*

Surface thermometer (Specific Transducer Corp., Model 311S); micropipets; capillary pipets, uncalibrated; filter paper for tape samplers (Whatman 41).



## 7. SAMPLING

Collect 0.1-2.0m<sup>3</sup> of air sample (depending on anticipated acid levels) with a sequential tape sampler providing either a one inch spot or a one-half inch sample spot. The sample spot is transferred in place on the tape to a ring oven for analysis.

## 8. PROCEDURE

Place the filter tape on the ring oven with the sample spot centered exactly over the annular space of the heated (90°C) surface. If a one-inch sample spot is taken, a ring oven with a 33mm diameter opening must be used. If a one-half inch sample spot is processed, a ring oven with a 22mm diameter ring should be employed. The following steps apply to the processing of the large sample spots. If the half-inch samples are being processed, then use only one-half the volume of reagents and solutions mentioned in the following procedure.

Add to the exact center of the sample spot 30μl of potassium bromide and wash to the ring zone with distilled water. Allow the ring to dry completely and then add 6μl of fluorescein. Wash the dye to the ring zone with methanol. Remove the tape from the ring oven and add potassium bromate solution around (from the outside!) the ring zone using a capillary tube. Return the tape to the hot ring oven with the spot centered as before and wait three minutes for full color development. Compare the color intensity of the ring with standard rings.

## 9. CALIBRATION CURVE

Standard rings are conveniently prepared by using 0, 2, 4, 6, 8, and 10μl of standard sulfuric acid solution. After the addition of the known amounts of standard acid, each spot is processed as described above. The resultant standard rings are stable for at least one month.

## 10. SPECIAL CASES

10.1 The procedure described anticipates the collection of samples by means of a paper tape sequential sampler. It is possible also to collect samples using high-volume samplers by processing only an aliquot of the total sample. For example, a one-half inch spot can be stamped out of the filter using a cork borer. With the dust spot down and centered on a piece of Whatman 41 filter paper (or S&S 495) the regular procedure described above can be followed. Calculations should take into account the fraction of the total sample being processed.



10.2 The procedure for sulfuric acid aerosol can be modified slightly to apply for the determination of total protons. Thus, not only are sulfuric acids measured, but protons from volatile acids, such as hydrochloric and nitric acids, and acid salts, such as ammonium sulfate, ammonium chloride and zinc sulfate, are included. The procedure in this case is as follows: Add to the center of the sample spot 30 $\mu$ l of potassium bromide and wash to the ring zone with distilled water. Allow the ring to dry completely and then add 6 $\mu$ l of fluorescein. Wash the dye to the ring zone area with methanol. Remove the tape from the ring oven and add potassium bromate solution around (from the outside) the ring zone using a capillary tube. Return the tape to the hot ring oven and wait three minutes for full color development. Compare the color intensity of the ring with standard rings.

## 11. REFERENCES

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