

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.

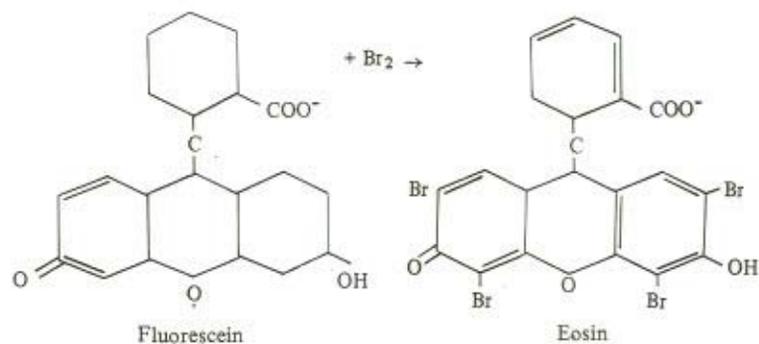
If non-volatile acid ( $H_2SO_4$ ) is to be measured the filter on which the sample has been collected should be heated at 100-105°C for 4 or more hours to eliminate any volatile acids.

## 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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