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RAPID FIELD TEST FOR FLUORIDES

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RAPID FIELD TEST FOR FLUORIDES

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INTRODUCTION

Numerous tests have been run on various types of methods for the past five years to find a rapid field method for the determination of fluorides as an atmospheric contaminant, particularly as fluorine might be connected with welding. The method of Willard and Winter was used a considerable period of time but was not satisfactory due in part to the time involved in the distillation to remove impurities. A satisfactory modification of the alizarin sodium sulphonate and zirconium nitrate method was evolved which, in our hands, was somewhat more satisfactory than the published methods, particularly from the standpoint of speed. However, the range of significance from the health standpoint involves concentrations from 1 to 10 p.p.m. and requires a more rapid determination in the area where operations are being performed than can be obtained by any method which involves carrying solutions back to the laboratory for analysis after spending from 15 minutes to 2 hours in collecting the air sample.

Some inorganic compounds of fluorine are gaseous and would require an estimation of the concentration within a few minutes so that safety and health requirements might be met.

Since methods involving the collection of a sample and the subsequent transport to a laboratory would not meet this requirement methods collecting the sample in a liquid medium with reagents present which would indicate the relative amounts of fluoride immediately were tried. While still working on this approach it was decided that the fastest estimation would be through the use of an indicating paper. Such papers can often be made to give semi-quantitative results by pumping known amounts of contaminated air through the chemically treated paper.[1]

Experiments were conducted with papers treated with sodium alizarin sulphonate and zirconium chloride but these were not as satisfactory even under ultraviolet light as those papers treated with zirconium salts and azo-arsenic acids. The paper finally determined upon was one treated with p-dimethylamine-azo-phenylarsenic acid and zirconium oxychloride[2]. In dilute acid solution an insoluble salt of zirconium azo-phenylarsenate, brown in color, is deposited in the pores of the paper. The excess of p-dimethylamino-azo-phenylarsenic acid is washed out with dilute acid. When fluorides are drawn through the prepared paper a colorless (ZrF_6) ion and the free azo-phenylarsenic acid which is red are formed. Thus we have a distinct color change from the brown zirconium compound to the red of the free azo acid and this has been made the basis for a semi-quantitative field method for the determination of the fluoride ion.

In very small quantities, such as is dealt with in determining concentrations injurious to health, fluorine itself is hydrolyzed to hydrofluoric acid and this is assisted by moistening the paper with hydrochloric acid. Soluble fluorides, such as sodium fluoride, react on the hydrochloric acid moistened paper to give an immediate fluoride ion reaction. The insoluble inorganic fluorides, such as calcium fluoride, are retained by the moist filter paper and react to give the typical fluoride reaction but not until a longer period of time has elapsed. The method is roughly quantitative in that values in the range from 6 to 10 p.p.m. can be determined within ± 1 p.p.m. and from 10 to 40 p.p.m. with decreasing sensitivity as the concentration of fluoride ion increases. In concentrations below 6 p.p.m. the method become increasingly less sensitive to each stroke of the pump and at 2 p.p.m. may be estimated within ± .2 p.p.m. The accuracy at the given concentrations is largely determined by the number of strokes of the calibrated pump. These concentrations were chosen because they were the most important in regard to health and safety.

PREPARATION OF CHEMICALLY TREATED PAPER

The treated paper is made according to Feigl and Rajmann[2] except for the washing of the paper which was done without the use of ether. Properly prepared, these papers are a light canary yellow when dry. Prior to insertion in the pump attachment head they are wetted with 2N HCl. The color changes to a light brown. After exposure to the fluoride ion a faint red-pink color appears.

INTERFERENCES

Those anions interfere which give insoluble or stable soluble complex compounds with zirconium. Organic hydroxy acids, arsenates, phosphates, sulphates and thiosulphates are included in this group. However, under the conditions of the test in the ranges set up, sulphates and arsenates do not interfere in amounts below 50 p.p.m. Using the calibration procedure to be described in a following section and testing for fluoride ion in concentrations from 2 to 10 p.p.m., no change in the amount of air taken through the test paper was noted where sulphate ion of 10 times the concentration of the fluoride was introduced into the test atmosphere. If sulphates are present in higher concentrations and no fluoride ion is present there is a reaction but the resultant color is a salmon pink instead of a red-pink. Under unusual conditions, sulphates do not constitute a serious interference but phosphates will interfere and will give approximately the same effect as the fluoride ion.

PUMP

A pump of 50 ml. capacity was chosen as this volume of air on preliminary crude calibration tests apparently would allow the greatest accuracy for the concentrations from 1 to 40 p.p.m. of fluoride ion which was the concentration of greatest interest from a health and safety viewpoint. A head to hold the test papers was built according to the attached drawing.* A plastacele insert holder 1¼ inches in diameter with a ¼ inch strip across the center provided an opening which permitted the air to flow through the paper at a rate which permitted standarization of the reaction of the fluoride ion with the test paper.

CALIBRATION

A 46.2 liter bottle was coated with a fine film of paraffin and volumetric measured amounts of 48% hydrofluoric acid were introduced in a paraffin block placed on the bottom of the bottle. The bottle closed with a 2-hole rubber stopper and 2 glass tubes connected to rubber tubing and a bulb completed the closed system. Air was circulated over the drop of hydrofluoric acid until it was dissipated throughout the jar. There was evidence that the distribution was not good but several tests were carried out which indicated that .03 c.c. of .1 to 100 solution of 48% hydrofluoric acid corresponding to 3.3 p.p.m. would give a reaction with 17 strokes of the pump. .03 c.c. or 5.6 p.p.m. fluoride gave a light pink with 10 strokes. When double this quantity of fluoride ion or 11.2 p.p.m. was evaporated a very slight reaction was noted with 5 strokes of the pump. When .01 c.c. or 1.1 p.p.m. evaporated, approximately 50 strokes were required to give a slight coloration.

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*Illustration - made by Production Equipment Co., [illegible] Cass Ave., Detroit, Michigan.

No quantitative significance could be attached to these results because of the inequalities of distribution and doubts as to the concentration of the concentrated hydrofluoric acid in our possession.

In order to more accurately determine the fluorine, $KF \cdot 2H_2O$ was weighed on a micro-balance in calculated amounts to give values ranging from .5 to 10 p.p.m. in the 46.2 liter bottle employed. This fluoride salt was placed in the hollow of a paraffin block and a drop of concentrated sulphuric acid dropped into the depression in the block after the bottle was closed up. The evolved hydrogen fluoride was recirculated throughout the bottle by means of a rubber bulb. Two separate determinations at 3 p.p.m. resulted in a very light pink coloration at from 4½ to 5 strokes of the pump in both instances. Later tests showed that distribution was not uniform and that this method of calibration would not give accurate results. Part of the fluoride would rapidly be removed on the wall surfaces and some would form a complex ion. The following system was then set up for the calibration of the treated paper.

To establish an atmosphere containing a definite value in parts per million HF, the dilute acid solution was atomized into a 46 liter bottle at a constant rate. The air-acid mixture was drawn from this bottle into a 630 liter chamber with an electrically driven air pump calibrated at .85 c.fm. Two combination impinger and fritted glass mist collectors were placed between the pump and large chamber with a set of T-tubes and pinch cocks. After pumping at a constant rate on one bubbler until the rate of flow and the parts per million HF become constant, the flow was switched to the second bubbler and timed with a stop watch. With the rate known in c.f.m. and with known time, the parts per million HF were established by titrating the acid solution in the second bubbler.

The titration was made with standard sodium hydroxide and potassium nitrate according to Scott's "Standard Methods of Chemical Analysis." 3 Without hydrofluoric acid the system shows a blank of 0.5 p.p.m. A comparison of the method with the thorium nitrate-alizaria titration shows a check within 0.5 p.p.m.

To establish a value in terms of number of strokes on the above described hand pump, the sample was taken from a T-tube by-pass attached just above the bubbler intake. While the air was passing at a constant rate, sufficient sample was drawn to give the first perceptible pink on the standard paper. The number of strokes required to do this is established before the titration is made, thus, there is a definite relation between this number and the p.p.m. HF determined later.

A series of 59 points were determined. Some of these show considerable distribution (Chart). However, it is definitely known that a portion of this is due to failure to establish a constant flow before switching to the second bubbler. Care must also be taken to avoid interfering gases in the laboratory such as ammonium hydroxide or hydrochloric acid.

For the calibration curve, all values in parts per million at a given number of strokes on the pump were averaged. Any values that varied ± 1 p.p.m. from this average were discarded and the average of the remaining factors used to establish the final curve. The calibration curve represents 61.5% of all points determined.

PRECAUTIONS

It has been observed in some preliminary work that uniformity of treatment of the paper employed is essential to get good results. We have found that a Whatman 41-H paper is most suitable for the test and the results specified were obtained

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when this paper was used. It was also noted that uniformity of deposition of chemicals upon the paper is important, and that it is essential to completely wash out all the excess p-dimethylamino-azo-phenylarsenic acid with great care before washing with alcohol and ether and drying in vacuo. Our paper was kept in a sealed vacuum chamber but there was apparently no great decomposition of our prepared papers if they were kept in sealed brown bottles when not in use. Tests made on papers prepared three months previously show them to be as sensitive as papers made the same day. It is not known how long these papers will keep at the present time but safety considerations dictate their replacement after this time until further test data is available. Treated papers exposed to light and oxidizing influences are not as sensitive as papers not so exposed but will give indications of concentrations of fluoride in the range of 6 p.p.m. but with great loss in accuracy after one week's exposure. Such exposed papers cannot be relied on.

FIELD TEST PROCEDURE

Prepared zirconium azo-arsenate paper is placed in the special fixture attached to a 50 cu. cm. pump. The paper is dipped into 2 N hydrochloric acid immediately before placing in the apparatus or in the field the paper may have previously been placed in the holder dry and enough acid added with a dropper just before using to wet the paper. Air is slowly drawn through the filter paper for a given number of strokes of the pump. It is recommended that a given number of strokes of the pump be taken so that quantities of fluoride which would be immediately hazardous may be determined immediately. If examined after 3 strokes of the pump in which 150 c.c. of contaminated air has been drawn through the paper and a reaction of greater or less intensity has occurred, it will be known that dangerous concentrations exist and immediate evacuation is indicated. If on removal from the apparatus the paper will show two very faint lips of pink coloration against the brown background, it will show the concentration to be 11 p.p.m. The first appearance of pink on the brown background is taken as the end point of the reactions. Should no pink appear the same paper may be replaced and another 5 strokes of the pump taken. By taking these strokes in groups of five it may be roughly determined after 18 strokes that no great danger exists as the concentration will be less than the 3 p.p.m. stated to be safe by the U S. Public Health Service. It is recommended that after the first examination of 3 strokes when it is determined that such danger does not exist as would cause immediate evacuation of the area, fresh papers should be used and about 17 strokes taken to see whether the U. S. Public Health Standard is approached. Any method useful in a particular situation may be used with calibration chart.

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