

## THE SAMPLING OF HYDROGEN FLUORIDE IN AIR WITH IMPREGNATED FILTER PAPER

C. HUYGEN

*Rijks Instituut voor de Volksgezondheid, Utrecht (The Netherlands)*

(Received January 1st, 1963)

In a previous paper<sup>1</sup> a method was described for the sampling of sulfur dioxide in air by drawing the air through impregnated filter paper. The filter paper was used to replace impingers or in combination with automatic filter tape air samplers. The impregnating liquids used were solutions of potassium hydroxide mixed with glycerol or triethanolamine. It is shown in the present paper that the same impregnated filters can be used for the collection of hydrogen fluoride in air.

Impregnated filter paper methods have been used previously for the estimation of fluoride in air. For instance, MILLER *et al.*<sup>2</sup> estimated fluoride in air by exposing limed filter paper to the air. An advantage of this method over the proposed method is its simplicity; a disadvantage is that a relatively long exposure time is necessary and that it is not easy to relate the sampled quantity of fluoride to the actual concentration in the air<sup>3</sup>.

KIELCZEWSKI<sup>4</sup> used the coloration by fluoride of filter paper impregnated with uranyl-iron(III) cyanide and THOMAS *et al.*<sup>5</sup> utilized the quenching of the fluorescence of magnesium oxinate on filter paper. These methods have the advantage that direct registration is possible, although this necessitates the use of a complicated measuring and recording instrument for each sampler; moreover, extensive calibration is necessary. Each of the methods mentioned will have its own field of application, that of the proposed method being principally its use in sequential samplers. The possibility of collection on an impregnated tape will simplify the construction of automatic samplers and analysers, and it can also be used with advantage instead of the impinger method in field work.

## EXPERIMENTAL

(1) Filters (Whatman no. 1, diam. 5.5 cm) were prepared by bathing them in the impregnating liquid, pressing off the excess, and drying them at 110°. As impregnating liquids were used solutions of 20% potassium hydroxide and 10% glycerol or triethanolamine in water. Some filters were exposed for a fortnight to air with a relative humidity of about 50% to imitate the condition of the filters after a long sampling time. After this treatment, the hydroxide in the impregnating solutions had changed about 50% into bicarbonate and 50% into carbonate, which seems to be nearly the equilibrium composition.

(2) The sampling procedure was as follows: the air containing hydrogen fluoride was drawn through the filters usually at a rate of 1 m<sup>3</sup>/h, the filters being clamped between plastic rings in a holder. The rings restricted the effective diameter of the filters to 4 cm, or in some experiments with high linear air velocity, to 1.5 cm. The experiments were generally conducted at room temperature.

(3) The collection efficiencies of the filters were determined from the quantities of hydrogen fluoride found respectively in the filters and in impingers containing 0.1 *N* sodium hydroxide placed in series. The collection efficiency of the impingers was found by the two-impinger method to be about 97%, which was nearly independent of the humidity or the air velocity.

(4) The air flows were measured by rotameters.

(5) Air streams of known relative humidity were obtained by mixing laboratory air of known humidity and air dried with silica gel.

(6) Air streams with different hydrogen fluoride concentrations were obtained by allowing the air to pass over different surface areas of 40% hydrofluoric acid. The concentrations were nearly constant with time and were calculated from the chemical analysis of the filters and impingers. Hydrogen fluoride in the gas phase may associate and it is uncertain which form was obtained by the method described; however, as will be seen below, the actual form in the gas phase is probably of little consequence.

(7) The hydrogen fluoride in the washings of the filters and in the impingers was determined after careful neutralization by the cerium-alizarin complexan method of BELCHER AND WEST<sup>6</sup>. This method is useful in the study of air pollution because it is little affected by sulfate.

## RESULTS

As in the case of sulfur dioxide, collection efficiencies were high at high humidities. The hydrogen fluoride was collected even more efficiently than sulfur dioxide. From Fig. 1 it is apparent that in the case of hydrogen fluoride the efficiency was practically 100% for freshly prepared filters at humidities above 25%. In this Fig. as well as in

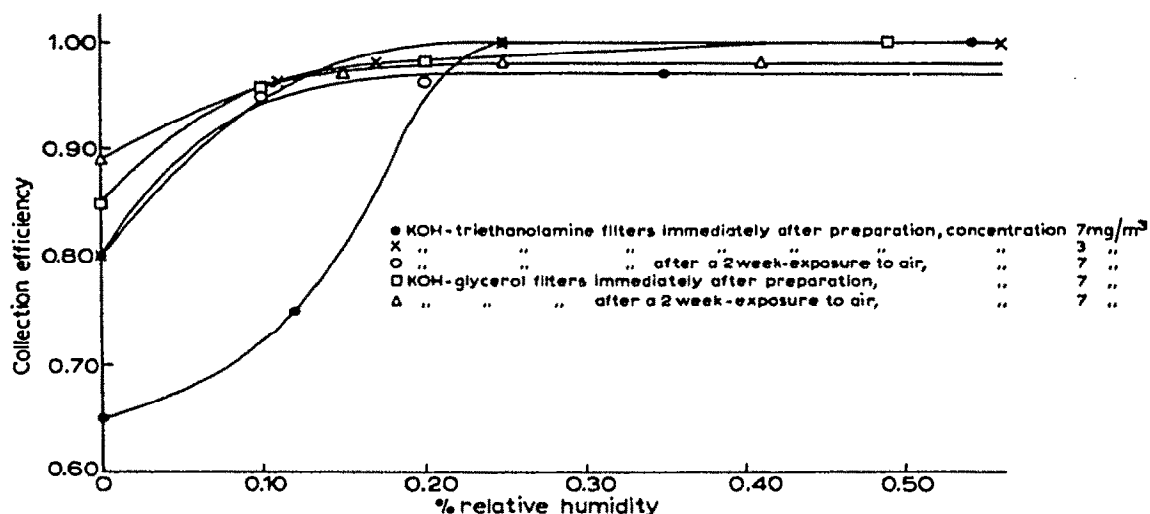
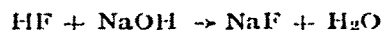


Fig. 1. Collection efficiency of different filters vs. the humidity at a linear air-velocity of 22 cm/sec and a sampling time of 10 min.

the others, each point represents the mean of two determinations. The previously exposed filters were somewhat better only at low concentrations and low humidities. The glycerol filters were slightly better than the triethanolamine filters at low humidities. It is rather remarkable that at 0% humidity, the collection efficiency could increase with increasing hydrogen fluoride concentration. For instance, at a concentration of 50 mg/m<sup>3</sup>, a collection efficiency of 87% was obtained with triethanolamine filters. This effect may be due to the formation of a better absorbing liquid with the water formed in the reaction



Here, as well as in the case of sulfur dioxide, the collection efficiency depended not only on the concentration and the humidity but also on the linear air velocity and the sampling time. This dependence is shown in Figs. 2 and 3.

In Fig. 2 the abscissa was chosen to represent not the linear air velocity, but the

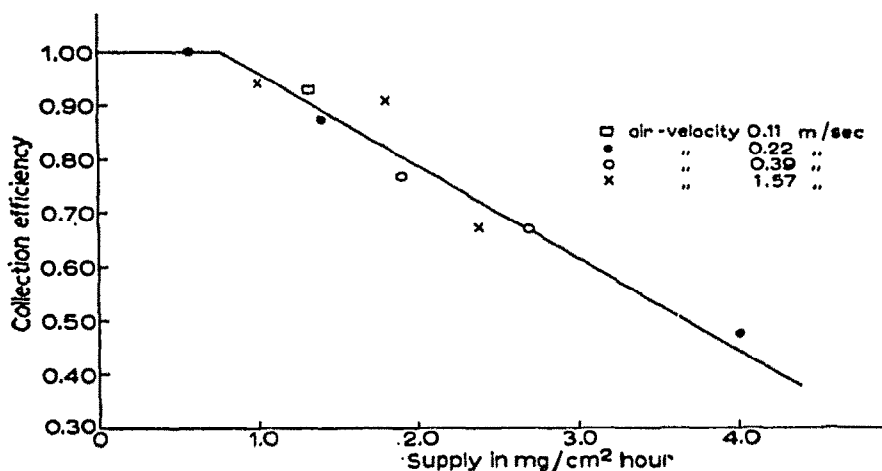


Fig. 2. Collection efficiency vs. the rate of supply of HF at different linear air velocities, a sampling time of 10 min and a humidity of 25%.

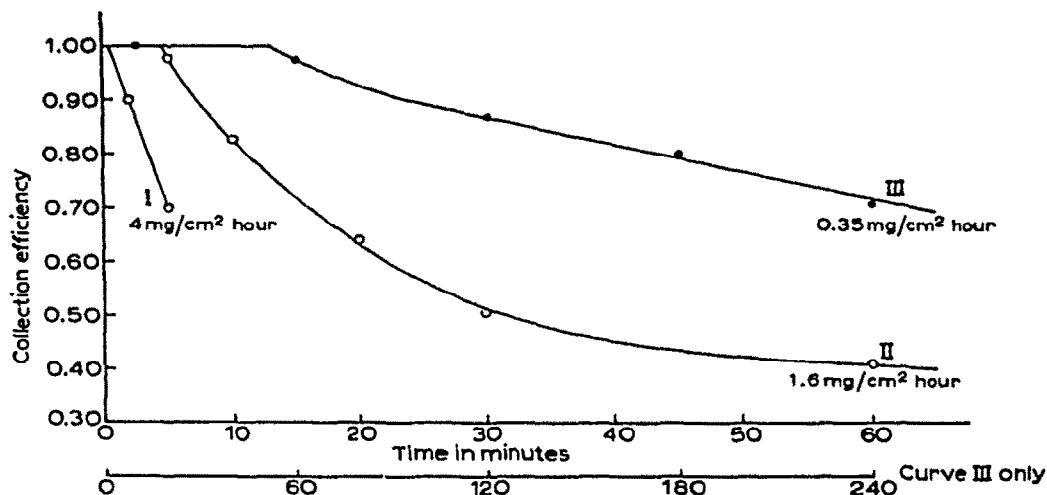


Fig. 3. Collection efficiency vs. the sampling time at different rates of supply at a relative humidity of 25%.

product of this variable and the concentration; this product may be called the rate of supply. This new parameter was introduced because the points in Fig. 2 then lay more or less on the same line. Thus it is apparent that the collection efficiency does not depend on the linear air velocity or on the concentration alone, but on their product — the rate of supply — which is the quantity of hydrogen fluoride arriving per unit time per unit filter area.

Figure 3 shows the dependence of the collection efficiency on the sampling time. As expected, there was a certain time of breakthrough dependent on the rate of supply. After the breakthrough point the efficiency dropped rapidly at high rates of supply and slowly at low rates of supply.

The results of some practical measurements of hydrogen fluoride in air near a superphosphate plant are given in Table I. No detectable amounts of fluoride were found in the impingers after the filters ( $< 1 \mu\text{g}/\text{m}^3$ ). The agreement between impinger and filter method was satisfactory.

TABLE I  
COMPARISON BETWEEN IMPINGER METHOD AND FILTER METHOD

$\mu\text{g HF}/\text{m}^3$ found by	
<i>Impinger method</i>	<i>Filter method</i>
0	0
19	18
14	12
39	39
42	44

#### DISCUSSION

In practical air pollution measurements, the concentration of hydrogen fluoride will generally be so low and the humidity so high (at least in Western Europe) that one can use the impregnated filter paper method without considering its limitations. This is true for long sampling times as well as for short sampling times; for it was found that filters which had been exposed to air for some time so that the sampling medium changed from the original potassium hydroxide to a mixture of carbonate and bicarbonate, were also quite efficient at low rates of supply.

It may be, however, that measurements of "high" concentrations are required, in which case the concept of the time of breakthrough may be useful; this is best illustrated by an example.

Suppose filters are used with an effective diameter of 4 cm and a sampling time of 1 h. The highest expected concentration is  $10 \text{ mg}/\text{m}^3$ , and the lowest expected humidity 25%. Now the time of breakthrough must not exceed 1 h, and from Fig. 3 it can be estimated that this corresponds to a maximal rate of supply of  $0.3 \text{ mg}/\text{cm}^2$ . This gives for the maximal sampling rate

$$\frac{\pi \cdot 4 \cdot 0.3 \text{ mg/h}}{10 \text{ mg}/\text{m}^3} = 0.38 \text{ m}^3/\text{h}$$

It is clear that the time of breakthrough depends not only on the rate of supply and the humidity, but also on the temperature and the presence of other (acidic) air pollu-

tants. It should be possible to predict this influence if sufficient knowledge about the mechanism of the absorption by filters were available. An indication is found about this mechanism in the observation that the collection efficiency does not depend strongly on the linear air velocity. This may be explained by assuming that the diffusion in the gas phase is so fast that the influence of variations in velocity can be neglected.

It would be worthwhile to do the (extensive) experimental and theoretical work necessary to gain a more complete insight.

#### SUMMARY

A method is proposed for the quantitative collection of hydrogen fluoride in air by drawing a known quantity of the air through filter paper impregnated with solutions of potassium hydroxide and glycerol or triethanolamine. Some possibilities and limitations of the method are discussed.

#### RÉSUMÉ

L'auteur propose une méthode de prélèvement de l'acide fluorhydrique dans l'atmosphère, par aspiration de l'air à travers un papier filtre imprégné. On utilise comme liquide d'imprégnation des solutions d'hydroxyde de potassium avec glycérol ou triéthanolamine. Les possibilités et les limites de la méthode sont discutées.

#### ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung des Fluorwasserstoffes in Luft vorgeschlagen. Die Luft wird dabei durch ein Filter gesogen, das mit einer wässrigen Lösung von Kaliumhydroxid und Glycerin oder Triäthanolamin imprägniert ist. Die Möglichkeiten und Grenzen der Methode werden diskutiert.

#### REFERENCES

- <sup>1</sup> C. HUYGEN, *Anal. Chim. Acta*, 28 (1963) 349.
- <sup>2</sup> V. L. MILLER, D. F. ALLMENDINGER, F. JOHNSON AND D. POLLEY, *Agriculture Food Chem.*, 1 (1953) 7.
- <sup>3</sup> D. F. ADAMS, *Intern. J. Air Water Pollution*, 4 (1961) 247.
- <sup>4</sup> W. KIELCZEWSKI, *Roczniki Chem.*, 30 (1956) 953.
- <sup>5</sup> M. D. THOMAS, G. A. ST JOHN AND S. W. CHAIKIN, *ASTM Special Technical Publication*, 250 (1959) 49.
- <sup>6</sup> R. BELCHER AND T. S. WEST, *Talanta*, 2 (1959) 92; 8 (1961) 853.

*Anal. Chim. Acta*, 29 (1963) 448-452