

COMPARATIVE STUDY OF METHODS FOR THE DETERMINATION OF AIRBORNE FLUORIDES

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ABSTRACT

Some current methods for the determination of both particulate and gaseous compounds of fluorine, present in air as pollutants, are described and compared. The operation included sampling of the air, the separation of fluoride from interfering substances and its final determination. Results obtained for the separation of fluoride by distillation and by other techniques of micro-diffusion are presented, as well as those obtained by the application of different methods to the subsequent determination of fluoride. The analytical method used by the authors is described, giving some results obtained in its application to the control of air pollution caused by an aluminium smelting plant.

In July 1966 we were asked to determine the extent of air pollution by fluorides caused by an aluminium plant in an area situated in the North of Italy. The whole study covered a period of two years, and followed the improvements introduced by the industry on the abatement system. Consequently, many hundreds of samples of air, stack effluents and other emissions have been analyzed, both for gaseous and particulate fluorides. To perform this task, the complete method of analysis, including sampling, separation and determination of airborne fluorides, was checked in each of these steps; we shall now try to give a brief report on the analytical conclusions we have been able to draw from this experience.

Considering first the operation of sampling, it is a well known fact that the collection of a representative sample is the hardest task of the entire analytical procedure when discrimination of gaseous and particulate fluorides is required, as was the case with our controls. The difficulties arise from the high reactivity of the hydrogen fluoride which tends to interact with the particulates always present in this type of emission. At the time when we faced this problem, several techniques had been applied to the separation of the gaseous compounds prior to the collection of particulates in an attempt to prevent this interaction (Pack and co-workers¹, 1960, Adams and co-workers², 1963), but the procedures were applicable to ambient air, while we had to sample also stack gases, which are characterized by a higher concentration of hydrogen fluoride, particulates and water as compared with samples of air. It was only in 1968 that a stack sampling technique for particulate and gaseous fluorides was reported by Dorsey and Kemnitz³. For practical reasons we decided to collect first the particulates and afterwards the gaseous fluorides, and from the proposed methods we decided to use membrane filters followed

by absorption in alkaline solution. The high efficiency of this type of filter for the collection of the particulate components of aerosols (near to 100 per cent), as well as their capacity to retain particles smaller than the diameter of the filter pores was at the time widely proved (Schadt and Cadle⁴, 1957). From tests made by Pack and co-workers⁵, sorption of gaseous fluorides in membrane filters does not reach 7 per cent, compared with 23.5 per cent sorbed by paper filters under the same conditions. To have an idea of the extent of retention of gaseous fluorides on the filters used (Millipore 0.8 μ , mean pore diameter), we made the following tests: filters containing different samples of particulate emissions or immissions from the aluminium plant were treated in the laboratory, as soon as possible, with a current of hot air to desorb the gaseous fluorides retained. Experiments were made by passing the air current through: (1) a Drechsel bottle containing 0.01 N NaOH for purification, (2) a column filled with silica gel for desiccation, (3) a heating chamber to raise the air temperature at 70°, (4) a Millipore filter and (5) two Drechsel bottles containing 50 ml of 0.01 N NaOH for sampling the desorbed fluorides; the mean time of this treatment is 15 minutes.

Table 1. Retention of gaseous fluoride by the membrane filter
(Millipore—mean pore size 0.8 μ)

Sample	Conditions and time of sampling	Collected gaseous fluoride (as F, in μ g)			
		In the absorbent solution (NaOH 0.01 N)	Desorbed from the filter	Total % F retained in the filter	% F retained in the filter
Stack effluent of Al-plant	<i>With no preheating</i>				
	(1) 15 min-40 litres	10.0	5.5	15.5	35.5
	(2) 15 min-40 litres	8.5	9.0	17.5	51.4
	(3) 15 min-40 litres	11.0	10.5	21.5	48.8
Air sampled at 1 km from the plant	<i>With no preheating</i>				
	(4) 25 h-7.5 m ³	78.0	2.0	80.0	2.5
	(5) 25 h-6.0 m ³	54.0	1.0	55.0	1.8
Stack effluent at Al-plant	<i>With preheating</i>				
	(6) 60 min-522 litres	39.0	2.0	41.0	4.9
	(7) 70 min-612 litres	41.0	1.0	42.0	2.4
	(8) 60 min-490 litres	170.0	6.5	176.5	3.7

^a Desorption made by passage of air which has been previously purified (bubbling in O, 1 N NaOH), dried (passage through silica gel) and heated to 70°.

Results in Table 1 indicate that the absorption of hydrogen fluoride in the filter can be, in practice, neglected in the case of air samples, but is extremely high for samples of stack effluents. The main difference between the two types of sample is the high water content of the stack effluents, which are practically saturated with water, and for this reason, in the case of stack emissions, we surrounded the filter holder with a small chamber electrically heated to keep the gas temperature to a value around 70°. The heating device was already used in the plant for the control of its emissions. Results from the application of the same technique of desorption to the stack samples thus obtained are also reported in the table. These results are reasonably acceptable, as only 5 per cent, as a maximum, of the gaseous hydrogen fluoride is retained in the filter. The preheating of stack gases in the sampling of parti-

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culates makes possible also the use of higher filtration velocities. The range of sampling velocity we have used is from 250 to 600 litres of gas per hour; only in a few cases was velocities of 100–200 litres of air per hour used.

In a very recent paper, Finkelstein, Polykovskaya and Morozova⁶ have established the best experimental conditions to carry out the filtration of particulates reducing to a minimum the hydrogen fluoride absorption in the filtrate. The conditions are: sampling velocity higher than 120 litres per hour and humidity of the sample lower than 90 per cent. By maintaining these conditions, the sorption of hydrogen fluoride on the filter can be kept below 5 per cent of the total amount of gaseous fluorides present.

For the collection of the gaseous products we used two Drechsel bottles each containing 50 ml 0.01 N NaOH. We have found it convenient to reduce the normality of the solution of alkali used from 0.1 to 0.01 N to facilitate subsequent concentration of the sample that might be necessary in the following step, in cases in which vary small quantities of fluorides are involved. In doing so we are supported by the statement of Farrah, who says that it makes little difference whether water or an alkaline solution is used as a collecting medium⁷.

Once the sample is obtained, the next step is to separate the fluoride from interfering substances, because no known analytical method is specific enough to eliminate this separation when the control of industrial pollution is concerned, due to relatively high amounts of other substances present in the sample. In fact, even the direct colour reaction methods based on the reaction with the cerium or lanthanum complexes of alizarin complexan, need masking or extraction steps to eliminate certain interferences, when they are present in amounts higher than certain limiting values.

In our case, the electrolytic aluminium plant used both cells with Soderberg anodes and cells with prebaked anodes. Consequently, emissions were formed by both gaseous and particulate components, the first being water, hydrofluoric acid, and traces of carbon tetrafluoride, sulphur dioxide, hydrogen sulphide, carbon dioxide and carbon monoxide, and the particulates being aluminium oxide, aluminium fluoride, sodium fluoride, cryolite, sodium and potassium sulphates, carbon and organic matter, with traces of other metallic elements.

To isolate fluoride we use both steam distillation with sulphuric acid and the microdiffusion processes.

The major disadvantage of steam distillation is the high operator time consumption and the fact that the isolated fluorides are obtained in very dilute solutions, not always suitable for direct determination when low concentration fluoride samples are analyzed. Furthermore when we checked the method, we soon realized that, for quantities of fluoride not higher than 10–15 μg , recoveries of known quantities of fluoride added were no better than 60–70 per cent. The first two disadvantages are overruled by the application of the microdiffusion technique reported by Singer and Armstrong⁸ in 1954, Frere⁹ in 1961, Hall^{10, 11} in 1960 and 1963 and in the OCDE's Methods of measuring air pollution¹² in 1964. In all these papers, the process has been applied to isolate amounts of fluoride from 0.1 to 20 μg as a maximum in the presence of perchloric acid. Even if it is not expensive from the point of view of operator time consumption, the actual separation includes

a period of 20 hours in a drying oven to obtain quantitative values for fluoride. Greenland¹³, in 1962, reported quantitative recoveries of amounts of 6 μg fluoride by substituting perchloric acid with sulphuric acid and by using small polythene cells modelled after the standard Conway type¹⁴. We intend, in the near future, to try the application of this method to air analysis.

Instead of the different kinds of microdiffusion cells reported (polythene bottle of Hall, polythene dish modelled after the Conway type¹⁴) we adopt the simple Petri dishes used by Zurlo for the separation of amounts of fluoride not higher than 20 μg . We have checked the process using dishes of 5 cm diameter and we did not find any reason to avoid the use of the common glass dishes, as we obtained quantitative recoveries with them.

Table 2. Recovery of fluoride through microdiffusion

<i>F added</i> μg	<i>F found</i> μg	<i>F recovered</i> %	<i>Interferent added</i>
as NaF:			
1.00	0.90	90	none
1.00	0.95	95	"
1.00	1.04	104	"
5.00	5.00	100	"
5.00	4.96	96	"
10.00	9.96	99.6	"
10.00	10.06	100.6	"
50.00	51.50	103.0	"
50.00	50.10	100.2	"
50.00	49.30	98.6	"
100.00	94.60	94.6	"
100.00	100.40	100.4	"
100.00	90.00	90.0	"
200.00	156.00	78.0	"
200.00	163.00	81.5	"
500.00	240.00	48.0	"
500.00	280.00	56.0	"
5.00	4.90	98.0	Al ³⁺ = 406 μg
10.00	10.30	103.0	Al ³⁺ = 406 μg
5.00	4.86	97.2	Cl ⁻ = 100 μg
5.00	5.03	100.6	Cl ⁻ = 500 μg
5.00	4.90	98.0	Cl ⁻ = 1.000 μg
5.00	5.05	101.0	Fe ³⁺ = 560 μg
10.00	10.25	102.5	Fe ³⁺ = 560 μg
as cryolite:			
5.96 ^a	6.21	104.2	—
14.9 ^a	14.40	96.6	—

^a Recovered by steam distillation.

The sample, in a volume not higher than 3 ml, is placed in the dish, and twice its volume of 70 per cent perchloric acid is added. The container is quickly covered with its lid (which has been previously prepared by evaporating in it 1–2 ml of an alcoholic solution of NaOH in a drying oven, at 50°, for 30 minutes). The covered containers are left in the drying oven, at 50°, for at least 20 hours. The fluorides in the cover are then extracted with a few millilitres of distilled water, the solution and the washing liquids being collected in a 10 ml volumetric flask and diluted to the mark with distilled water.

We found most suitable the use of lids containing 4 mg deposited NaOH, as a precaution in case small amounts of chlorides are present in the material

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microdiffused. In any case, distillation of chlorides can be avoided by adding a small amount of solid Ag_2SO_4 to the container. Recoveries of known amounts of fluoride obtained by varying the ratio of sample to acid volume, indicated that, as reported by Hall, the 1:2 ratio gives quantitative values, but we also find that similarly good results are obtained by the use of 1:3 or 1:4 ratios. Recoveries of fluoride through the microdiffusion process carried out under these conditions, as well as those obtained in the presence of some of the major components of the sample aerosol that might interfere with the spectrophotometric determination, are reported in Table 2. From results in the table we can see that under the conditions described microdiffusion can separate amounts of up to 100 μg with at least 95 per cent recovery.

It may also be noticed that, with the experimental conditions described, the upper limit for the amount of fluoride that can be separated by microdiffusion has been raised to 100 μg instead of 20 μg .

Any attempt to shorten the time of diffusion (by altering temperature and concentration of acid) failed. Recoveries of fluorides in amounts ranging from 2 μg to 100 μg are not quantitative before 20 hours of diffusion. Two curves of fluoride recoveries as a function of diffusion time, for two different amounts of added fluoride, are given in *Figure 1*.

The application of the microdiffusion process to our samples is made directly by placing the Millipore filter containing the particulates in the microdiffusion dish, covering it with 2 ml of distilled water and using the following procedure.

For the microdiffusion of the gaseous fluoride samples, a 50 ml aliquot of the alkaline solution from the Drechsel bottle is concentrated to 1–2 ml, transferred to the microdiffusion dish, and washed with 1 ml of distilled water.

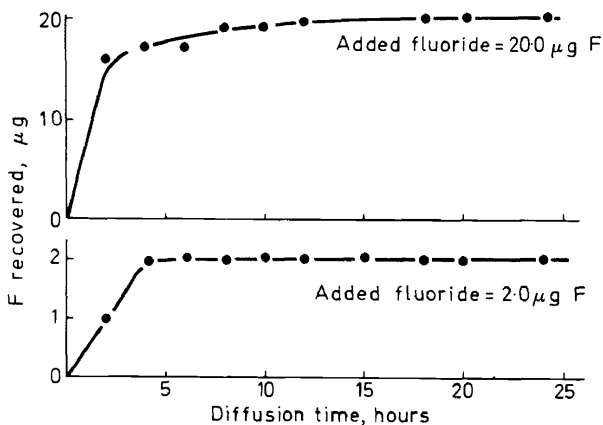


Figure 1. Recovery of fluoride as a function of diffusion time.

For the quantitative determination of the fluoride content of the 10 ml solution obtained, we use spectrophotometric methods.

Having in mind its high sensitivity we started by using the OCDE's method¹² which is based on Belcher's reaction; the formation of a fluoro-chelate

with lanthanomalizarin complexonate mainly for samples of low fluoride concentration^{16,17}. This method has a range of application from 0 to 30 μg fluoride; many of our air samples were far more concentrated in fluoride due to the fact that sampling was continued for 24 hours with a final volume of air taken which often was higher than 10 m^3 ; the stack gas samples were of small volume but also highly concentrated in fluoride. For this reason we have also used a method studied by one of us for the determination of fluorides in water¹⁵, scaling down the quantities of sample and reactant to adapt it to the range of concentrations found in air analysis. The method is based on the decolouration of the alizarin-zirconium lake and it is very suitable for routine determination because of its extreme simplicity: to a known volume of sample is added 1/10th of its volume of the reagent. The reagent is a solution of alizarin-zirconium lake in which the concentration of components have been fixed to obtain the maximum sensitivity: zirconium 0.0004 M, alizarin 0.0008 M, sulphuric acid 1.35 N (see *Figure 2*). The optical density of the reaction can be measured at any time after two hours, provided that the reaction times for the sample and the standard do not differ by more than 15 minutes. We found it easier, when a large number of samples are analyzed, to leave the samples and the standards in contact with the reagent overnight, in order to make the readings independent of the reaction time (after this period the colour is invariable.).

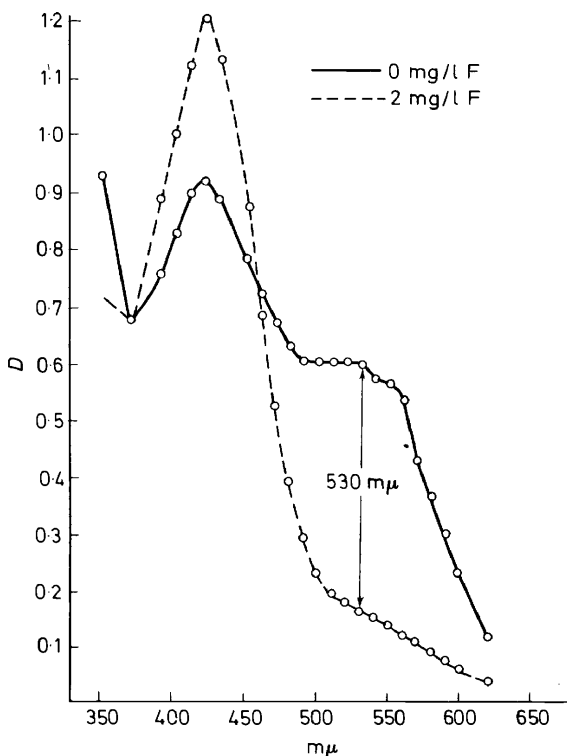


Figure 2. Absorption curve for the standards containing 0 and 100 μg fluoride in 50 ml (lake alizarin-zirconium spectrophotometric method).

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Using a 10 ml sample, with 1.0 ml of reagent, the method allows the determination of fluorides in the range from 0.20 to 20 μg , with an accuracy of $\pm 0.06 \mu\text{g}$, while using a 50 ml sample with 5.0 ml reagent, amounts from 0.5 to 100 μg can be determined with an accuracy of $\pm 0.25 \mu\text{g}$ (see *Figure 3*).

In a certain number of samples we have divided the 10 ml solution obtained from microdiffusion into two aliquots: in one of them, fluorides were determined by the alizarin-zirconium method while in the other by the OCDE method.

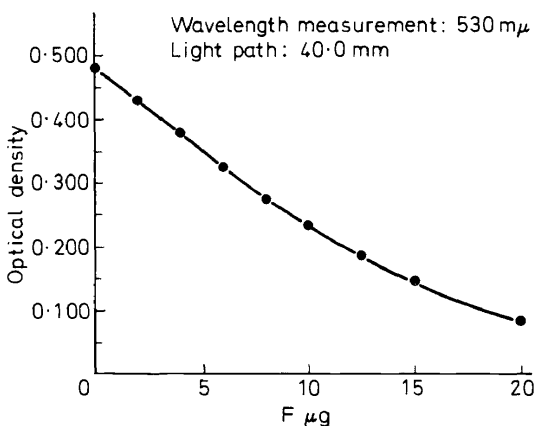


Figure 3. Calibration curve for 10 ml sample and 1 ml reagent (lake alizarin-zirconium spectrophotometric method).

Results obtained by the two methods are in good agreement. The OCDE method has a better sensitivity and is more reliable for the smallest concentrations of fluoride: the alizarin-zirconium method has a far wider range of application. Our experience in the field of measurement of atmospheric pollution of industrial origin indicates that, when an aluminium smelter is involved, the mean amounts of fluoride collected, in an area surrounding the plant of 5 km diameter, are in general higher than 5 μg , with values as high as 375–500 μg for 24 hours sampling. Stack emission and Martigny emission samples have, of course, even higher amount of fluoride. This is the reason why we made our choice of the alizarin-zirconium method for routine determination in the particular case of aluminium smelting pollution.

DISCUSSION

R. Truhaut: If I understand you correctly, you were trying to control air pollution from an aluminium smelting plant. May I ask you where this plant was located?

Author: The plant was located on the west bank of the river Adige, which in this zone flows through a narrow Alpine valley. The intervention of the Institute of Health was requested by local authorities in view of the state of pollution, presumably by fluorides, observed in an area nearly 3–4 km from the plant. In this area signs of relevant damage to grapes were evident and,

what was far more important, the economic losses were accompanied by the presence of typical dermic lesions in the human population, mainly in women and children. The complete results of the study are being published in a separate paper.

R. Truhaut: Did you, by any chance, make fluoride determinations in the urine of the exposed subjects and, if so, what were the results in relation to the levels of fluoride found in the air?

Author: We found concentrations of urinary fluoride (expressed as fluoride ion) ranging from 0 to 1 mg/l in 54.5 per cent of the exposed subjects, from 1 to 2 mg/l in 25 per cent of the subjects and from 2 to 3 mg/l in 13.6 per cent of the subjects; values of 5.7, 4.4 and 3.9 mg/l were found in three cases. The fluoride concentrations in air in the same period were (24 hs mean values): 0.001 and 0.043 mg/m³ respectively for gaseous and particulate fluoride 0.3 km north of the plant; 0.001 and 0.025 mg/m³ respectively for gaseous and particulate fluoride 1.0 km of the plant south and 0.001 and 0.019 mg/m³ respectively for gaseous and particulate fluoride 2.5 km south of the plant.

J. Monkman: Were the microdiffusion vessels used made of glass?

Author: The recovery experiments were quantitative, which of course validates the use of glass in this instance.

J. Monkman: Do you use a sealing agent with the glass Petri dishes?

Author: No sealing agents were used since they had not been found necessary and they require additional manipulation.

J. Monkman: Yes, we also used plastic dishes without a sealing agent, in fact it was found that the sealing agent could contain more fluoride than the sample itself.

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