

Methods for measuring chlorides and fluorides in waste gas emissions from glass melting tanks



A report by Technical Committee 13, Pollution, of the International Commission on Glass

The Technical Instructions on Air Quality Control published in the Federal Republic of Germany in 1986 contain emission limits for 'vapourous or gaseous inorganic substances'. The emission limit for chlorine and its vapourous or gaseous compounds, expressed as HCl, is 30 mg/nm³ at 8% oxygen for sources with a mass flow of more than 0.3 kg/h. The limit for gaseous fluorides, expressed as hydrofluoric acid, is 5 mg/nm³ at a mass flow of material of more than 50 g/h. The same or similar emission limits are being discussed and introduced in other Member States of the European Economic Community.

Such low emission limits are a potential problem for glass manufacture. Fluoride raw materials are used in some glass compositions to assist the melting and refining processes; the manufacture of continuous glass fibre and opalescent decorative glasses are examples of glass making processes which use fluorides. However, even more seriously, chlorides and fluorides are present at low levels as impurities in common glass making raw materials such as dolomite, saltcake (sodium sulphate), and soda ash (sodium carbonate). Adventitious emissions arising from the impurity content can also exceed the emission limit values.

The accurate measurement of low concentrations of chlorides and fluorides in glass making waste gases has become an important matter for glass manufacturers and the regulatory authorities. This paper is intended to summarise and compare the different methods of measuring chlorides and fluorides which are used in the glass industry and to draw conclusions about preferred methods. Technical Committee 13 has also published a similar paper on particulate measurement.⁽¹⁾

Chlorides and fluorides in glass making

As additives

Chlorides are only occasionally used as batch additives. Sodium chloride has been used in certain glass compositions as a source of sodium, but other sodium compounds are preferred. It is used as a refining agent for borosilicate and special glasses made under reducing conditions.

Fluoride raw materials used in the glass industry

are fluorspar, calcium fluoride, and, occasionally, cryolite and sodium hexafluorosilicate.

In opalescent glasses the final fluoride content in the glass is about 0.6 wt%. To compensate for volatilisation during melting about 1 wt% of fluoride must be added to the batch. Fluorides are also used in the manufacture of borosilicate E glass.

The emission of fluorides from a 9 tonne per day tank with 0.8% fluorspar in the batch is of the order 60 mgF⁻/nm³.⁽²⁾ As a melting and refining agent in, for example, the manufacture of continuous glass fibre, some 0.9% of the batch is fluorspar and about 0.4% of the fluoride is retained in the glass. A typical fibre furnace with a throughput of 120 tonnes of glass per day, and a waste gas volume of 15 500 nm³/h, will have an emission of about 80 mgF⁻/nm³ at 8% O₂. Both these examples would exceed the TA Luft limit values.

The environmental effects of fluoride emissions from a glass fibre works have been reported by Bulcraig.⁽³⁾

As impurities in raw materials

The ranges of chloride and fluoride contents of common glass making materials, from different geographical sources, are shown in Table 1. Estimates of chloride and fluoride emissions arising from these impurities in typical batches and typical Cl⁻ and F⁻ retentions in the glass, for large container or flat glass furnaces, indicate emission concentrations and mass emissions which exceed the TA Luft thresholds.

Table 1. Ranges of chloride and fluoride contents (ppm) of glass making raw materials (see, for example, References 4, 5, and 6)

Raw material	Cl ⁻	F ⁻
Sand	20-330	30-60
Dolomite	10-2200	120-400
Limestone	25-600	30-160
Sodium carbonate	60-2800	6-120
Sodium sulphate	4-40	2-40
Feldspar	40-190	8-60
Colemanite	-	100-300
Nepheline syenite	10	40-370
Cullet	100-300	20-800
Slag	100-4500	70-1800
e.g. Calumite	500	3300

Chloride and fluoride balances

A chloride or a fluoride balance may be calculated from a typical batch for a glass furnace based on the impurity content of raw material, the Cl⁻ or F⁻ retained in the glass, and the mass emissions of these pollutants. Table 2 illustrates, first, that chloride and fluoride emission concentrations can approach or exceed the emission limits now in force in West Germany and, second, that the difference between the calculated and the measured emissions can be large. Investigations have been carried out to try to determine whether discrepancies arise from the methods of analysis of the glass and raw materials or the methods of sampling the waste gases.

Measured chloride and fluoride emissions

Examples of measured emission concentrations of chlorides and fluorides from different glass making furnaces are presented in Table 3 which shows the wide range of chloride and fluoride concentrations which may be emitted from glass making furnaces using raw materials obtained from different sources. With the exception of the fibre and borosilicate glasses, neither chlorides nor fluorides are used as deliberate additives, yet there are significant emissions of these pollutants.

Table 2. Chemical balances for a 213 tonne/day container furnace fired with natural gas

<i>Fluoride and chloride in raw materials (%)</i>		
	Cl ⁻	F ⁻
Dolomite	0.0658	0.014
Sodium sulphate	0.0024	0.00018
Sodium carbonate	0.277	0.0012
Chromium oxide	0.0916	-
Sand	0.0031	0.0030
Slag	0.323	0.00475
Limestone	0.0216	0.016
Cullet	0.033	0.0080

<i>Furnace conditions</i>		
Load	213 tonne/day	
Cullet	42.5%	
Waste gas volume	18472 nm ³ /h	

<i>Chloride</i>		
<i>Balance (kg/day)</i>	<i>In</i>	<i>Out</i>
Raw materials	134.165	-
Glass	-	105.185
Emission by difference	-	28.98

<i>Emission (mg/nm³)</i>		
calculated	-	65.36
measured	-	21.60

<i>Fluoride</i>		
<i>Balance (kg/day)</i>	<i>In</i>	<i>Out</i>
Raw materials	13.62	-
Glass	-	12.78
Emission by difference	-	0.84

<i>Emission (mg/nm³)</i>		
calculated	-	1.89
measured	-	1.12

Table 3. Measured chloride and fluoride emissions (mg/nm³) from different glass making furnaces at 8% oxygen

Fuel	Glass	Load (t/d)	Cl ⁻	F ⁻	
Gas	Container				
	green	330	40	4	
	yellow green	300	180	<1	
	green	120	120	35	
Oil	Container				
	green	280	110	43	
	green	140	50	10	
	yellow green	290	60	12	
Gas	amber	-	2	13	
	flint	120	100	7	
	flint	120	89.5	0.82	
	Fibre	120	9	80	
	Oil	Float	700	18	4.0
	Oil	Float	600	50	3.3
	Gas	Float	700	15	4.1
	Gas	Float	600	39	5.7
	Gas and oil	Borosilicate			
		(NaCl refined)	120	320	-

Methods of measuring chlorides and fluorides in glass making waste gases

Principle of the method

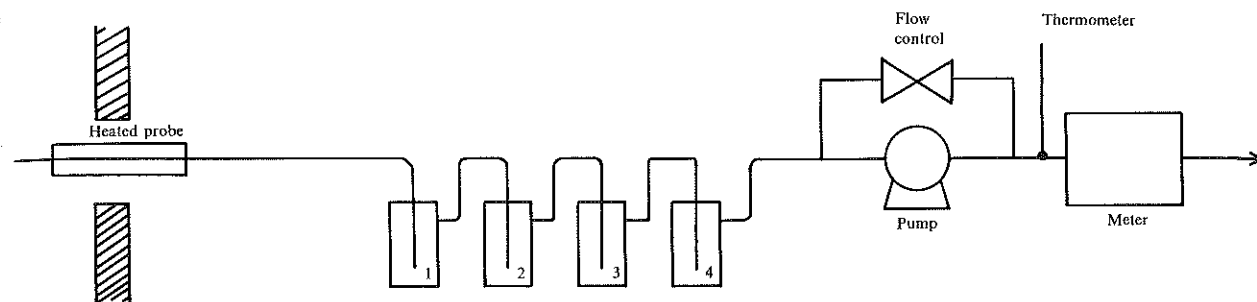
The method is similar for both chlorides and fluorides. A known volume of a representative sample of flue gas is drawn through a filter (if it is necessary to determine separately the particulate and gaseous fractions) and then a gas absorption train: the filter is omitted if only a total figure is required. The chloride and fluoride content is determined by analysis of the absorbing solutions and the filter residue.

The sampling train

The basic sampling trains are shown diagrammatically in Figures 1-4, Figures 1 and 2 being the trains for the determination of total chloride and fluoride respectively and Figures 3 and 4 those for the simultaneous determination of gaseous and particulate chloride and fluoride or for the gaseous components only.

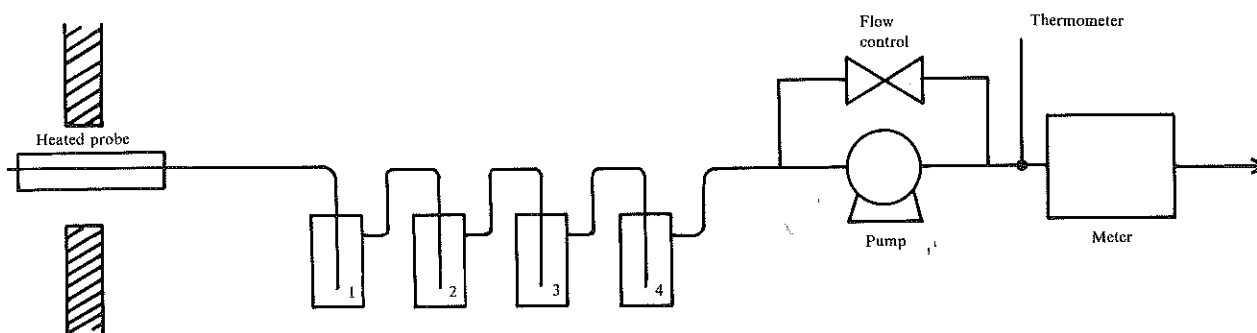
The trains consist of a quartz, stainless steel, or Hastalloy sampling tube of approximately 8 mm internal diameter and long enough to take representative samples of hot flue gases from a duct. This probe should be a material which does not react with the waste gases and therefore stainless steel is often preferred. To prevent the condensation of acid gases, the probe is heated either directly or indirectly using a simple heat exchanger jacket which circulates the hot flue gas.

The sampling procedure may be simplified by removing the filter and collecting both the solid and gaseous components in the absorption train (Figures 1 and 2). Alternatively, where it is necessary to determine the particulate content or the gaseous components separately, a probe with a detachable quartz wool filter is used (Figures 3 and 4). The absorbing liquids in the bottles or impingers are water or



Country	Cell 1	Cell 2	Cell 3	Cell 4	Isokinetic	Sampling rate
UK	H ₂ O (or 3% H ₂ O ₂)	H ₂ O	Empty	Silica gel	Yes	—
Germany	H ₂ O	H ₂ O	H ₂ O	Empty	Yes	100 litres in 30 min (VDI guideline 3480)
Italy	0.1 NaOH	0.1 NaOH	0.1 NaOH	Silica gel	No	—
France	Empty	0.1 NaOH	0.1 NaOH	0.1 NaOH	Yes	—
USA	H ₂ O	H ₂ O	Empty	Silica gel	Yes	Minimum 30 min

Figure 1. Sampling train for the determination of total chloride



Country	Cell 1	Cell 2	Cell 3	Cell 4	Isokinetic	Sampling rate
UK	0.1 NaOH	0.1 NaOH	Empty	Silica gel	Yes	—
Germany	0.2 NaOH (with 3% H ₂ O ₂)	0.2 NaOH	0.2 NaOH	None	Yes	100 litres in 30 min (VDI guideline 2470)
Italy	0.1 NaOH	0.1 NaOH	Empty	Silica gel	No	—
France	Empty	0.1 NaOH	0.1 NaOH	0.1 NaOH	Yes	—
USA	Empty	0.1 NaOH	0.1 NaOH	Silica gel	Yes	Minimum 30 min

Figure 2. Sampling train for the determination of total fluoride

hydrogen peroxide solution for chlorides and sodium hydroxide solution for fluorides. The location and temperature of the filter, the number and content of the absorbers or impingers, and the rate of sampling are possible variables in the method. In some cases regulatory authorities have standardised these details, for example the German VDI 3480 *Measurement of hydrogen chloride* (1984) and VDI 2470 *Measurement of gaseous fluorine compounds* (1975).

Methods of analysis

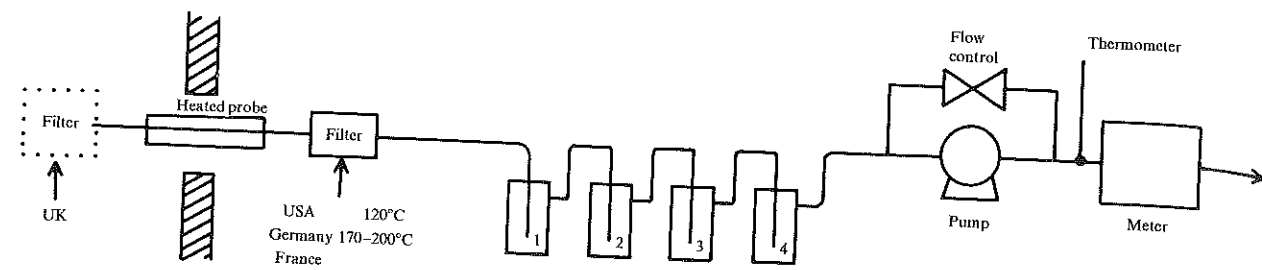
Analysis of absorbing solutions. To determine the amount of chloride or fluoride collected in the train the volume of absorbing solution is measured. The solution is then buffered to pH 5.8 and analysed using either a fluoride ion specific electrode or potentiometric titration for chloride. The concentration of

fluoride is determined by comparison with known standards.

The concentration of chloride or fluoride in the flue gas is determined from their concentrations in the absorbing solutions and the waste gas volume which is drawn through the sampling train.

Alternatively, Cl⁻ and F⁻ concentrations may be determined using ion chromatography. The impinger solutions are mixed and a quantity aspirated into an ion chromatograph. The concentration of each ion is determined by comparing the height of the Cl⁻ and F⁻ peaks with those from standard solutions.

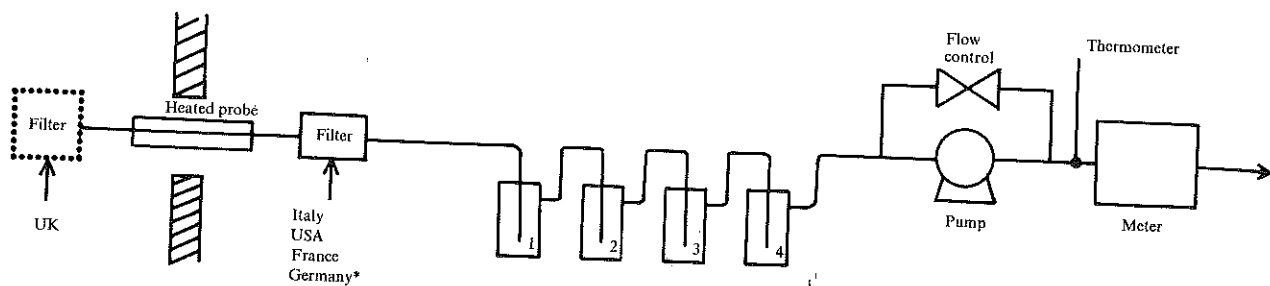
Analysis of the glass and raw materials. A range of analytical methods is used to determine the chloride and fluoride contents of glasses and raw materials. Basically the halogen is extracted by fusion and washing, by pyrohydrolysis, or by acid extraction. The



Country	Cell 1	Cell 2	Cell 3	Cell 4	Isokinetic	Sampling rate
UK	H ₂ O (or 3% H ₂ O ₂)	H ₂ O	Empty	Silica gel	Yes	—
Germany	H ₂ O	H ₂ O	H ₂ O	None	No*	100 litres in 30 min (VDI guideline 3480)
France	—	0.1 NaOH	0.1 NaOH	0.1 NaOH	Yes	—
USA	Empty	H ₂ O	H ₂ O	Silica gel	Yes	Minimum 60 min

*Particulate content not measured separately

Figure 3. Sampling train for the simultaneous determination of gaseous and particulate chloride



Country	Cell 1	Cell 2	Cell 3	Cell 4	Isokinetic	Sampling rate
UK	0.1 NaOH	0.1 NaOH	Empty	Silica gel	Yes	—
Germany	0.2 NaOH (with 3% H ₂ O ₂)	0.2 NaOH	0.2 NaOH	None	No*	100 litres in 30 min (VDI guideline 2470)
France	0.1 NaOH	0.1 NaOH	0.1 NaOH	Silica gel	Yes	—
USA	Empty	0.1 NaOH	0.1 NaOH	Silica gel	Yes	—

*Particulate content not measured separately

Figure 4. Sampling train for the simultaneous determination of gaseous and particulate fluoride

chloride or fluoride in solution is then determined by chromatographic potentiometric titration (for Cl⁻) or ion sensitive electrode (for F⁻) analysis. To compare these methods a round robin investigation was undertaken. Seven laboratories were invited to determine the Cl⁻ and F⁻ contents of nominally identical samples of Float glass and the results of this investigation are tabulated in Table 4 which shows that a wide range of values may be obtained using standard analytical techniques. This throws into question the reliability of Cl⁻ and F⁻ balances calculated from the analyses of raw materials and glass.

Mass balances for halides. The variations shown in Table 4 may be used to illustrate the consequent discrepancy which would arise in a mass balance calculation assuming that typical raw materials analyses are correct. The following calculation would be typical for a 5000 tonne per week, gas fired, Float glass furnace using 25% cullet:

	Minimum	Typical	Maximum
Cl ⁻ retained in glass (%)	0.0075	0.0115	0.080
Chloride in (kgCl ⁻ /h)			
Batch	4.2	4.2	4.2
Cullet	0.6	0.9	6.0
Total	4.8	5.1	10.2
Chloride out (kgCl ⁻ /h)			
Glass	2.2	3.5	28.8
Waste gas (by difference)	2.6	1.6	-13.6
Total	4.8	5.1	10.2
Cl ⁻ at 8% O ₂ (mgCl ⁻ /nm ³)	29	18	—
F ⁻ retained in glass (%)	0.0015	0.0040	0.0081
Fluoride in (kgF ⁻ /h)			
Batch	1.8	1.8	1.8
Cullet	0.1	0.3	0.6
Total	1.9	2.1	2.4
Fluoride out (kgF ⁻ /h)			
Glass	0.5	1.2	2.4
Waste gas (by difference)	1.4	0.9	0
Total	1.9	2.1	2.4
F ⁻ at 8% O ₂ (mgF ⁻ /nm ³)	16	10	0

Table 4. Results of a round robin analysis of Cl⁻ and F⁻ contents of nominally identical samples of Float glass

Laboratory	Cl ⁻ (%)	Method	F ⁻ (%)	Method
1	0.012 ±0.004	Acid extraction: silver electrode	0.003 ±0.0005	DIN 51084 ion sensitive electrode
2	0.013 0.0135 0.0115	Pyrohydrolysis: ion chromatography Pyrohydrolysis: ion sensitive electrode XRF	0.004 — —	Ladd-Peters ion sensitive electrode — —
3	0.016 0.020 0.019 —	Fusion: colorimetric Fusion: colorimetric Fusion: colorimetric —	0.0071 0.0081 0.0061 0.0044	Fusion: ion sensitive electrode Fusion: ion sensitive electrode Fusion: ion sensitive electrode Pyrohydrolysis: ion sensitive electrode
4	— 0.013 ±0.01 0.06 0.08 0.08	— Silver titration Ion sensitive electrode Ion sensitive electrode Ion sensitive electrode	0.0062 0.0025 — — —	Pyrohydrolysis: ion sensitive electrode Ion sensitive electrode — — —
5	0.0113 0.014 0.0153	Silver potentiometric Silver potentiometric Silver potentiometric	— — —	— — —
6	0.0075 0.0075	Colorimetric Colorimetric	0.0033 0.0029 0.0026	Ion sensitive electrode Ion sensitive electrode Ion sensitive electrode
7	0.01	Silver nitrate titration	0.008	Pyrohydrolysis: ion sensitive electrode
8	0.01	Silver nitrate titration	0.003	Pyrohydrolysis: ion sensitive electrode
Range	0.0075–0.080		0.0015–0.0081	
Average	0.025		0.004	

Chemical balance calculations of the Cl⁻ and F⁻ emission for this furnace would give values of 0 and 29 mgCl⁻/nm³ for chlorides and 0 and 16 mgF⁻/nm³ for fluorides arising from the maximum and minimum analyses of retained Cl⁻ and F⁻.

The sampling method

Total chloride or fluoride. The sampling trains shown in Figures 1 and 2 are used, the probe being positioned at a representative traverse point in the duct and a known volume of gas drawn through the train at a flow rate of between 1 and 2 litre/min. The test procedures may then differ. In West Germany and United States the flow of gas through the probe is adjusted to maintain isokinetic conditions. In France, Italy, and the United Kingdom the flow is adjusted to a suitable rate to collect sufficient pollutant for analysis in a sampling time of 20–30 min.

The details of the train also vary, notably in the number and order of absorption bottles/impingers and in their content. Figures 1 and 2 summarise the principal variables in sampling trains used by laboratories in different European countries for the measurement of Cl⁻ and F⁻ emissions from glass works chimneys.

Gaseous and particulate chlorides or fluorides. The sampling train shown in Figures 3 and 4 is used. In this method the probe contains an alumina or quartz filter which may be located in the duct at the temperature of the waste gas or outside the duct at ambient or a controlled temperature. To determine the particulate fraction accurately, sampling must take place under isokinetic conditions.

Investigation of the variables in the sampling train

The number of absorption bottles. A series of experiments was performed using the sampling trains of

Figures 2 and 4 to determine the efficiencies of fluoride collection in three absorption bottles. The tests with filters used a heated alumina thimble filter. The absorption efficiency of each bottle is shown in Table 5 together with the mass of F⁻ collected in each bottle, and these results suggest that, when sampling gases containing a high concentration of F⁻, the first bottle is an efficient collector but that, with a low concentration of F⁻ in the waste gas (e.g. test 4), a significant amount of fluoride may be found in the second and third absorber bottles. It seems possible that some fluoride may pass through the system and in such cases it may be necessary to use more than three bottles in the absorbing train.*

Comparison of a quartz probe, with and without washing, and a stainless steel probe. The waste gases from a borosilicate glass furnace were sampled for chloride and fluoride. In one series of measurements an unheated quartz probe was used and the probe was washed. Table 6 shows the Cl⁻ and F⁻ collected in the impingers and the total in the impingers plus

*To avoid analytical problems, the pH of the absorbing solution must be adjusted according to standard procedures.

Table 5. Efficiencies of collection of fluoride in three absorber bottles containing 0.1 N NaOH solution

Bottle		1	2	3
<i>Without filter</i>				
(1) Mass	(µg)	7500	183	180
Collected	(%)	95.3	2.4	2.3
(2) Mass	(µg)	8400	185	174
Collected	(%)	95.5	2.1	2.0
<i>With filter</i>				
(3) Mass	(µg)	905	132	49
Collected	(%)	83.3	12.2	4.5
(4) Mass	(µg)	375	84	64
Collected	(%)	71.7	16.1	12.2

Table 6. Comparison of measured concentration of Cl^- and F^- (mg/nm^3) obtained with a quartz probe with and without washings of and an unheated stainless steel probe without washing

	Quartz	With washings	Stainless steel
<i>Furnace 1 Natural gas fired, borosilicat glass</i>			
Cl^-	34.5	45.9	23.9
Cl^-	28.1	41.4	25.0
F^-	42.7	85.9	33.0
F^-	55.1	93.4	36.8
<i>Furnace 2 Oil plus natural gas fired, borosilicate glass</i>			
Cl^-	4.25	6.75	18.4
Cl^-	6.0	8.5	7.1
Cl^-	3.2	12.4	5.2
Cl^-	2.6	11.8	6.4
F^-	5.1	28.1	5.4
F^-	7.55	32.6	6.8

washings. At the same time the gases were sampled with an unheated stainless steel probe which was not washed: in all other respects the sampling trains were the same.

The large amount of Cl^- and F^- collected in the quartz probe and subsequently washed out indicates that unheated probes should not be used and if using an unheated probe, the washings must certainly be included. When washing a stainless steel probe the analysis of the washings proved difficult because of the presence of corrosion products, which indicates that it is preferable to use a quartz probe. However, there is also a reaction between the hydrogen fluoride in the waste gas and a quartz probe but, if the probe is heated, the silicon tetrafluoride which is formed goes to the wash bottle. If a fluorine ion electrode is sensitive to all the fluoride, then the measurement of the fluoride emissions is not affected. If some fluoride ions remained complexed to silicon in the solution, and if the electrode is not sensitive to complexed ions, then an error will be introduced into the analysis and hence into the measurement of the emission.

Comparison of two heated quartz probes, one with and one without a filter. Measurements of HCl and HF were made simultaneously in the flue gas of an oil fired flat glass tank with two quartz glass probes with and without filter at almost the same position in the flue. Table 7 shows the concentrations of Cl^- and F^- analysed in the absorption solution: the close agree-

Table 7. Comparative measurements of HCl and HF in the waste gases from an oil fired flat glass tank (mg/litre of absorption solution)

Sample number	Cl		F	
	Without filter	With filter	Without filter	With filter
1	7.44	5.67	0.64	0.63
2	5.67	6.03	0.54	0.56
3	—	6.38	—	0.57
4	—	5.14	—	0.52
5	5.85	5.85	0.62	0.62
6	4.79	4.96	0.51	0.52
7	4.96	4.96	0.46	0.52
8	5.58	5.67	0.51	0.57
9	5.14	5.14	0.47	0.54
10	5.85	5.85	0.56	0.58
	5.69 ± 0.83	5.56 ± 0.49	0.54 ± 0.07	0.56 ± 0.04

ment between the results obtained with and without a filter, for both chloride and fluoride, shows that, for this type of furnace, the method which measures the total Cl^- or F^- (Figures 1 and 2) and the method for the gaseous components (Figures 3 and 4) give virtually the same result, though the error in the measurement is lower in the method with the filter.

Comparison using a filter inside the stack and a heated filter outside the stack. Simultaneous measurements were carried out by two laboratories with different sampling methods but the same procedures for the analysis of the absorption solutions. In both cases a heated probe was used with, in one case, a silica wool filter inside the stack and, in the other case, a heated silica wool filter outside the stack.

Table 8 shows the chloride emission measurements and Table 9 the fluoride emission measurements made on a gas fired flat glass tank. The results show good agreement between the two methods but this would not, of course, have been the case if the external filter had not been heated.

Both laboratories analysed a certain number of the absorption solutions used in the chloride measurements to test the reproductibility of the analytical procedures and Table 10 shows that good agreement can be obtained by laboratories using different sampling and analytical procedures.

Table 8. Comparison of chloride emission measurements (mg/nm^3) with a filter inside the stack (method 1) and with a heated filter outside the stack (method 2)

Measurement	Method 1	Method 2
1	16.4	16.8
2	18.9	16.0
3	16.3	15.4
Mean value	17.2	16.1
Mean value at 8% O_2	15.6	14.6

Table 9. Comparison of fluoride emission measurements (mg/nm^3) with a filter inside the stack (method 1) and with a heated filter outside the stack (method 2)

Measurements	Method 1	Method 2
1	0.28	0.27
2	0.12	0.20
3	0.11	0.19
4	0.10	—
Mean value	0.15	0.22
Mean value at 8% O_2	0.14	0.21

Table 10. Comparison of the analyses of the chloride absorption solution (mg/sample)

Sample	Laboratory 1	Laboratory 2
Untreated flue gas		
1	3.55	3.47
2	3.30	3.10
3	3.35	3.28
4	3.15	3.08
Cleaned flue gas		
1	2.48	2.38
2	2.51	2.44
3	2.10	1.98
4	2.72	2.69

Comparison of absorbing solutions. In the results reported in Tables 8 and 9, different solutions were used in the absorbing bottles. Method 1 used a sampling train consisting of two wash bottles containing demineralised water as the absorbing solution for chloride and a mixture of 70 ml 0.2 N NaOH and 15 ml H₂O₂ (3%) in each bottle for fluoride. Method 2 used a 1 N NaOH solution for both chloride and fluoride.

In another series of experiments carried out on a flat glass furnace fired with a mixture of gas and oil, the amounts of Cl⁻ and F⁻ determined by NaOH (0.1 N) and H₂O₂ (3%) absorbing solutions are shown in Table 11.

Table 11. Comparison of chloride and fluoride collected in different absorbing solutions (mg/nm³)

Solution	Cl ⁻	F ⁻
NaOH (0.1 N)	24.1	0.37
H ₂ O ₂ (3%)	24.7	0.25

Discussion

Any method for measuring the concentration of chlorides and/or fluorides in the waste gases from glass making furnaces must be capable of being used in a wide variety of circumstances, which include measurement on furnaces which may use chlorides or fluorides as deliberate additives and on furnaces where the emissions arise simply from impurities in the raw materials. The investigations reported in this paper have established some of the principles and some of the problems of measurement.

General experience shows a variability of ± 15% in the results but a limited number of results suggests that this may be reduced to ± 7-8%. The principal variables in the sampling method which have been investigated are

1. the number of absorbing stages in the sampling train
2. the material and the temperature of the probe
3. the presence or absence of a filter in the probe
4. the temperature of the filter
5. whether the probe washings are included
6. the sampling rate:

the method of analysis has also been investigated.

Calculated emissions from chemical balances have been compared with measured emissions to establish if emissions can be predicted from the Cl⁻ and F⁻ contents of the raw materials less the amount retained in the glass. The results suggest that large errors may result, due primarily, it would appear, to errors in the analysis of the Cl⁻ and F⁻ retained in the glass and, presumably, in the raw materials.

Variables in the sampling train

Number of absorbing stages. The trains most commonly used have either two or three absorbing stages. The results suggested that if the amount of chloride or fluoride in the waste gas is high then two stages will

remove up to 98% of the pollutant. However, if the concentration in the gas is low, as much as 12% of the pollutant may pass through even a third bottle. For the low concentrations now specified in emission limit regulations a minimum of three absorbing stages should be used.

Material and temperature of the probe. The most commonly used materials are quartz and stainless steel. Evidence of attack, particularly by fluoride, has been established on quartz probes but if the probe is heated, the silicon tetrafluoride passes into the absorption bottles and the accuracy of the result may be unaffected. Stainless steel probes can be used if the probe is heated to prevent condensation and hence corrosion; in general a heated probe should be used for the sampling of chlorides and fluorides.

Presence or absence of a filter. The comparison of results from an oil fired Float glass furnace suggests that a filter makes little difference to the total pollutant collected. Care must of course be taken to ensure that all particulate material collected on the filter is taken into solution.

The use of a filter is necessary if it is wished to determine the particulate and gaseous components separately; it is also desirable if the particulate burden of the waste gas is high.

Temperature of the filter. If a filter is used it should be situated inside the duct at the temperature at which the gas is being sampled; if situated externally the filter (and the probe) should be heated.

Inclusion of probe washings. The results of this investigation and general experience shows that the probe washings must be included in the analysis if the probe is not heated. Substantial errors will be introduced if this is not done.

Sampling rate. The rate at which the gas is taken through the solutions has not been studied in detail but experience suggests that in the determination of total pollutant it is not a critical variable within reasonable limits. For example, the results shown in Tables 8 and 9, which are very similar, were obtained at sampling rates of 3.3 litre/min (method 1) and 10 litre/min (method 2).

Isokinetic sampling

If it is wished to determine the particulate component separately or the total Cl⁻ and F⁻ then isokinetic sampling must be used. If it is wished to determine only the gaseous component this is not necessary.

Methods of analysis

The source of greatest error revealed by this study is in the analysis of chlorides and fluorides in the glass. The results of the round robin survey reported in Table 4 show a wide discrepancy between determination of the Cl⁻ and F⁻ content by different laboratories in the same glass. If this is also the case in the analysis of the raw materials, then major discrepancies will arise in establishing chemical balances for glass tanks.

Conclusion

Careful attention to all aspects of sampling and analysis is needed to obtain agreement between calculated and measured emissions of Cl^- and F^- .

A principal source of error in sampling arises from the use of unheated probes, particularly if the probe washings are not included. With this exception, errors introduced by variations in the sampling method appear to be secondary to analytical errors.

The principal source of error in calculating emissions occurs in the analysis of the Cl^- and F^- retained in the glass, and presumably in the raw materials.

A joint study of Cl^- and F^- sampling and analysis should be undertaken by ICG Technical Committees 2 (Analytical Methods) and 13 (Environmental Problems) to clarify the sources of possible error.

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Appendix

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