

Selenium emissions from glass melting furnaces: formation, sampling and analysis

A position paper by the Technical Committee 13, "Environment", of the International Commission on Glass (ICG)

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The ICG Technical Committee 13 (TC13 "Environment") have reviewed the methods for sampling and analysing selenium emissions from glass furnaces. Selenium is an important constituent of some types of glass but unfortunately, due to its high volatility, much of the selenium added to the batch of such glasses leaves the furnace in the waste gases. Accurate sampling, and subsequent analysis, of the selenium in the emissions are important both to understand its environmental impact and because its presence in waste gas is often controlled by statutory limits. This position paper assesses selenium emissions in relation to its unique chemical properties and describes how understanding these are required to understand waste gas chemistry, determine appropriate sampling methods, and to produce an accurate mass balance for selenium through the melting and emission processes. Methods for analysing selenium in waste gas flues, in the glass product and in particulate control filter samples are described and compared. The results of "round robin" tests are reported, and best practice methods for sampling and analysing selenium are suggested.

1. Introduction

NB In the following Nm^3 refers to a cubic metre at 0°C and a pressure of 1 atmosphere (101 325 Pa) under dry conditions.

Among the activities of the ICG Technical Committee 13 (TC13 "Environment"), assessment of analysis and measurement techniques for the characterization of solid and gaseous emissions from glass melting furnaces is one of the main topics. Measuring methods for particulate emissions, fluorides and chlorides and

sulphur oxides have been assessed in the past.

One of the components sometimes present in the waste gases of glass melting furnaces is selenium and its compounds. Selenium is widely used as a decolourising agent in flint soda–lime–silica glass production, and for colouring flat glass (automotive and architectural bronzes and greys) and artistic glass (red, yellow and orange colours). In addition, the large amounts of mixed recycled cullet used in the production of container glass can accidentally bring selenium into the batch.

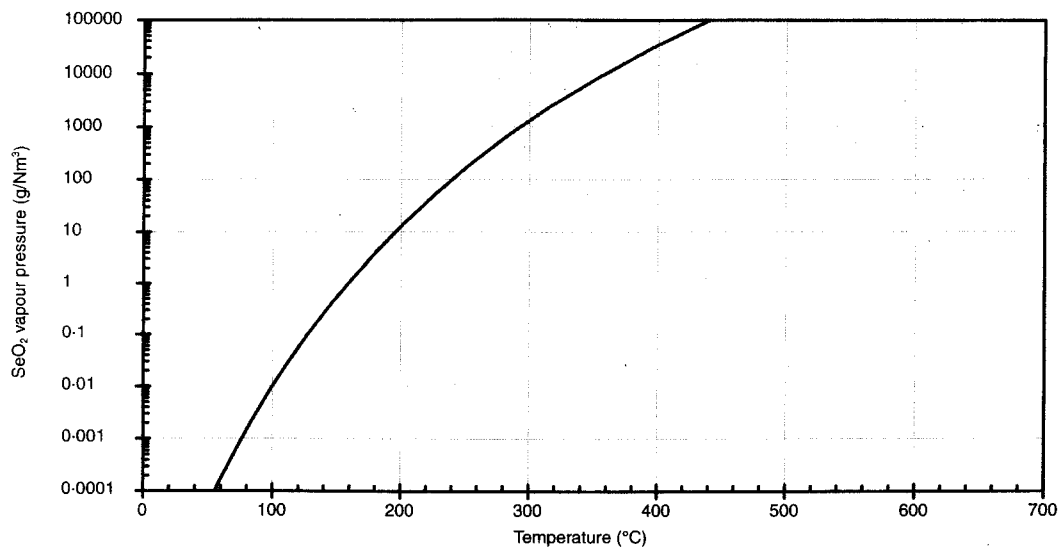


Figure 1. SeO_2 vapour pressure as a function of temperature

Emission limit values for selenium in the European Union refer to the total concentration (particulate and gaseous compounds) and can vary from 0.5 to 5 mg/Nm³, expressed at 8 % oxygen and in dry flue gas. In some countries, they apply when the mass flow is above 5 g/h. Such low limits can be hard to achieve for the glass industry, requiring very high removal efficiency by the scrubbing and filtration systems when selenium is used in the batch composition.

The accurate sampling and measurement of selenium in the waste gas is required to determine the emissions and assess compliance with the limits. These are difficult tasks because of the general characteristics and chemical nature of the selenium compounds evaporating from glass melting furnaces.

This paper summarizes and compares different sampling methods for selenium emissions and analytical procedures for the determination of selenium in different types of samples (glass, electrostatic filter dust, and sample absorption solution) with the objective of calculating accurate selenium balances for soda lime glass furnaces.

2. Use of selenium in the glass industry

Selenium compounds are used in the glass industry for both colouring and decolourising the glass, depending on its different oxidation states. The raw materials used for adding selenium to the batch composition are normally metallic selenium (Se^0), zinc selenite and sodium selenite. As a decolourising agent, selenium is retained in the glass at concentrations <2 mg/kg (ppm), while higher values are needed for colouring the glass, normally above 20 mg/kg (ppm), often in combination with other metals, such as iron, cobalt, or nickel.

2.1 Thermodynamic aspects of selenium vaporization and condensation in the flue gas of glass melting furnaces

Selenium is often regarded as a heavy metal, but its chemical behaviour is more similar to sulphur than that of typical metals. This must be taken into account when measuring selenium emissions. In general, selenium compounds are very volatile and tend to evaporate from the glass melt in significant amounts; up to 95% of the total selenium added to the batch may volatilise. This characteristic can result in high concentrations of selenium emissions in the flue gases of glass tanks. This selenium is predominantly in the gaseous form for gas temperatures above 200°C, which is the case in most situations (when no absorbing powder is injected). In order to better understand the behaviour of selenium in the flue gas, thermodynamic calculations were made using the HSC[®] thermodynamic calculation program (Version 5.1, Outokumpu, Finland, 2002).

2.1.1 Practical observations

It is well-known that selenium, in the flue gas, vaporizes as $\text{SeO}_2(\text{g})$, because this component is known to have a very high vapour pressure and it forms easily from Se^0 (often used in the glass batch), under the influence of atmospheric oxygen. In Figure 1 the vapour pressure from pure selenium oxide is shown for a wide range of temperatures, indicating that gaseous selenium compounds could still be found at temperatures as low as 60°C. This means that operation below this value is required during the selenium collection phase of measuring procedures in order to ensure that all flue gas selenium compounds are collected.

In a scrubber/filter secondary emission control

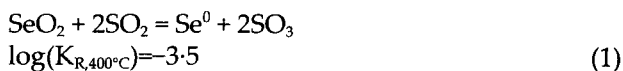
system, used to treat the flue gas with absorbing agents such as Na₂CO₃ or Ca(OH)₂, the SeO₂ typically reacts to form selenates (Se⁶⁺). The dust collected from the filter normally appears white. It is sometimes rose-coloured due to chemical reduction of some of the selenium components to elementary selenium, Se⁰, by the SO₂ present.

2.1.2 Thermodynamic explanation

According to the HSC[®] database, SeO₂ reaches atmospheric pressure at 315°C and due to its capability to sublimate at very low temperatures (see Figure 1), a theoretical vapour pressure of 1 mg/Nm³ of selenium (as Se or SeO₂ gas species) can be measured at 85°C. This concentration is equivalent to the emission limit value applied in some European Countries.

This indicates that selenium removal from the flue gas could be achieved by simple filtration only at very low temperatures, unless a dry absorbing reagent is used, or a wet scrubbing system is applied to form selenic acid (SeO₂*aq, "H₂SeO₃").

In agreement with observations, calculation shows that SeO₂ is not reduced by SO₂ in the gas phase, except at very low temperatures (below ~120°C), according to the following reaction:



The boiling point of Se⁰ is 685°C so it is typically condensed. The respective constant for gaseous Se⁰ is log(K) = -15.2. The reaction constant at 400°C, K_{R,400°C} is very low in reaction (1), making it difficult to separate out selenium as Se⁰. Furthermore, the formation of SO₃ and its condensation as H₂SO₄ droplets is kinetically hindered (although thermodynamically privileged). In contrast, if water and H₂SO₄ condensation is possible (e.g. in a sampling line), the reduction takes place and elementary red selenium (Se⁰) will condense in the form of fine particulate matter. This may occur at temperatures up to about 300°C, the maximum condensation point of sulfuric acid in flue gases. Dew points of flue gases are typically up to 160°C. This reaction also takes place in a heated probe if one is used for the sampling procedures; hence the probe must be washed out (to collect the deposited selenium compounds) and the washings collected in order to obtain correct results. On the other hand, in the flue gas the only gaseous selenium component is SeO₂.

The addition of alkaline reagents to the flue gas (e.g. calcium hydroxide Ca(OH)₂, sodium carbonate Na₂CO₃, sodium bicarbonate NaHCO₃), to remove gaseous acid pollutants, involves the reaction between different species, in the presence of CO₂, H₂O(g), and ~8% O₂ from air leakages. According to HSC[®], SeO₂ gas is transformed into selenates (Se⁶⁺)

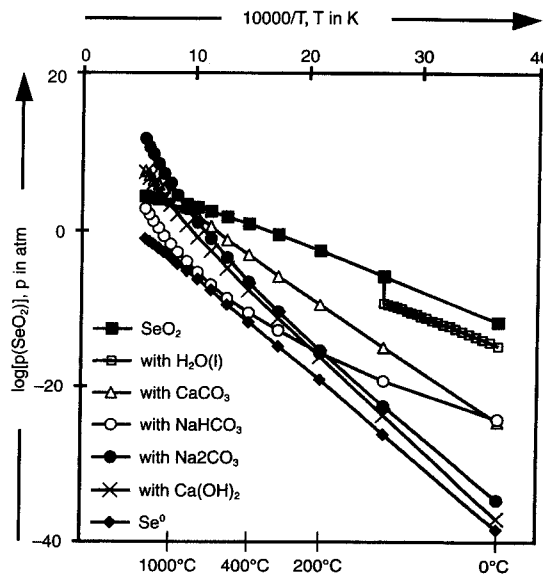
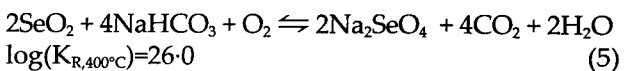
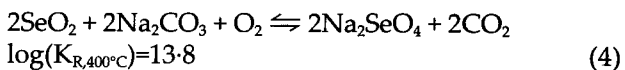
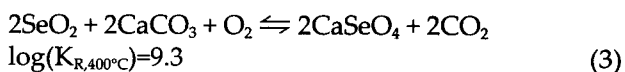
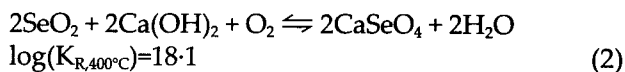


Figure 2. SeO₂ vapour pressure in flue gas of a glass melting furnace, calculated under different conditions

as follows:



A high value of logK_R means a high conversion level to the products on the right hand side of these reactions. The diagram in Figure 2 shows thermodynamically calculated values of SeO₂ vapour pressure under different flue gas conditions: the pure substance, the substance in contact with different absorbing reagents, and, as a comparison, the vapour pressure of pure elementary selenium under inert conditions (i.e. in absence of any oxidizing or reducing agent).

Table 1 below summarizes the vapour pressure values of SeO₂, in terms of log(p) values, as a result of the reactions (2) to (5) above, with the different

Table 1. Vapour pressure of SeO₂, calculated for different alkaline reagents added in excess and for a standard composition of glass furnace flue gas (10% CO₂, 10% H₂O and 8% O₂)

T (°C)	Reagent					Se ⁰
	Na ₂ CO ₃	NaHCO ₃	Ca(OH) ₂	CaCO ₃	SeO ₂	
200	-15.4	-15.6	-16.2	-9.5	-2.5	-19.2
400	-6.5	-10.5	-7.5	-3.1	1.0	-11.7
1000	6.0	-1.6	3.3	4.7	3.8	-3.4
1500	11.7	2.8	7.5	7.6	4.4	-0.9

reagents, as a function of selected temperatures. The vapour pressure of Se^0 above pure Se is also given for comparison.

As a reference, 1 ppm SeO_2 (v/v) is equivalent to $\log[p(\text{SeO}_2)] = -6$, and to 3.5 mg Se/Nm^3 in the flue gas. In comparison, the limit for selenium compounds given in the German TA Luft (2002) regulations for the glass industry, is 3 mg Se/Nm^3 , corresponding to $\log[p(\text{SeO}_2)] = -6.07$.

The temperatures in the table were chosen for the following reasons:

- (a) Waste gas filter systems are mostly operated between 200°C and 400°C,
- (b) The batch melting process takes place from around 1000 to 1200°C,
- (c) The refining process of the glass melt reaches temperatures up to ~1500°C.

Note that CaCO_3 is seldom used directly as an absorbing reagent. However, $\text{Ca}(\text{OH})_2$ partly reacts with the CO_2 present in the flue gas to form CaCO_3 and the absorption of SeO_2 by hydrated lime can be limited by this competitive reaction. Similarly, the reaction between Na_2CO_3 or NaHCO_3 and SO_2 takes place to form Na_2SO_4 and this is much more stable than Na_2SeO_4 . Other competitive reactions are represented by the formation of calcium and/or sodium chlorides and fluorides from HCl and HF present in the flue gas. Because of these possible competitive reactions, it is always necessary to add the absorbing reagent in excess of the selenium present to reach satisfactory removal efficiency.

Figure 1 and Table 1 indicate that the vapour pressure of elementary selenium (Se^0) is the lowest of the other compared species. This suggests that Se^0 would be retained by a filter used for the flue gas treatment. However, the low level of reducing substances and the presence of a relatively high amount of oxygen in the flue gas limit the formation of Se^0 and favours the presence of SeO_2 .

On the other hand, at glass melting temperatures, the vapour pressure of Se^0 is usually sufficient to cause significant amount of volatilization, with a typical loss between 60% and 95% of the selenium present in the batch. At this temperature, the vapour pressure of all other selenium components (calcium and sodium selenate, and also zinc selenide, zinc selenite, etc.) is significantly higher than that of Se^0 . This indicates that under slightly oxidizing conditions (i.e. a high level of excess air in the batch charging area) the emissions from the glass melt are not influenced by the type of selenium compound used in the batch composition, since SeO_2 will be the form evaporating from the melting glass and the material losses will always be high. Special precautions have to be taken in order to minimize these losses.

In theory, at 200°C, the vapour pressure of pure SeO_2 would correspond to about 1000 mg Se/Nm^3 .

The reaction between SeO_2 and the alkaline reagents added to the pollution control system causes a dramatic decrease in the concentration of selenium in the flue gas, with very low values, sometimes almost below the detection limit of the measuring methods. In practice, the absorption rate is limited by the following factors:

- (a) The competitive reactions mentioned above;
- (b) Reaction kinetics and diffusion rate of SeO_2 inside the porous particulates of the solid absorbing reagent.

Based on the above considerations, it must be noted that the calculated vapour pressure values, reported in Figure 1 and Table 1 represent theoretical lower limits; in practice the real measured values are higher, due to slow reaction rates. In practice, the most efficient reagent to remove Se at 200°C is sodium bicarbonate (NaHCO_3).

At 400°C, diffusion rates and reaction kinetics are much faster, but so are the competitive reactions. The equilibrium pressures come closer to the theoretical predictions, but, depending on the individual substances, reaction rates are always limited by the reaction kinetics and diffusion rates. Also in this case, the calculated values are to be considered as lower limits, with one exception: the calculated value for CaCO_3 predicts an equilibrium pressure of 800 ppm Se (v/v). In this case the competing reaction to form CaCO_3 is very slow and does not influence significantly the removal efficiency of SeO_2 from the flue gas. The most efficient alkaline reagent for removing gaseous selenium at temperatures about 400°C is calcium hydroxide ($\text{Ca}(\text{OH})_2$).

3. Selenium emissions to air

Selenium emissions can vary significantly, based on the quantity of raw material used in the batch composition. The amount of selenium added for use as a decolourising agent is based on the impurities contained in the batch composition (e.g. chromium and iron), in order for it to compensate for a yellow-green colour with a pink colour. The typical residual concentration of selenium in such glass varies from 0.5 to 2 ppm Se. The use of selenium for colouring glass bronze or grey can result in a concentration up to 130 ppm in the glass.

Table 2. Typical emission concentration ranges of Se in waste gases from glass melting tanks for different types of glass

Type of glass	Selenium emissions as Se Un-cleaned flue gas mg/Nm ³ , dry at 8% O ₂	Cleaned flue gas mg/Nm ³ , dry at 8% O ₂
Flint glass	0.8-25	0.1-3
Green container glass	0.2-0.8	<0.1
Bronze flat glass	15-40	0.5-3

Table 3. Emission limit values for selenium in furnace waste gases in some European countries

Country	Limit values applied in European countries		Reference	Note
	Concentration (mg/Nm ³)	Mass flow (g/h)		
Germany	3		at 8% O ₂ , dry	When selenium is necessary for product quality
France	1		at 8% O ₂ , dry	
	3		at 8% O ₂ , dry	When used for colouring or decolourising
Italy	1	5	at 8% O ₂ , dry	
United Kingdom	5		at 8% O ₂ , dry	In total, with As, Co, Ni, Cr ⁶⁺
The Netherlands	1		at 8% O ₂ , dry	
	3		at 8% O ₂ , dry	When selenium is used as a raw material
Belgium	0.5	5	at 8% O ₂ , dry	In total with Co, Ni, Te
(Walloon region)				
Proposal 2006	3			When used for colouring or decolourising

As previously explained, most of the selenium added to the batch will evaporate during the melting process causing emissions to air if not controlled, the concentrations of which vary significantly with the type of glass produced. The melting of bronze glass, and in most cases, the production of flint glass, generates concentrations of selenium emissions well above the typical emission limit values applied in Europe. As a consequence, it is necessary to remove most selenium compounds from the flue gas by means of a treatment system, normally consisting of a filter equipped with a scrubber/absorption stage. Knowledge of the reaction kinetics and the chemical behaviour of selenium are essential for choosing the most suitable conditions for achieving high removal efficiencies. Typical emission concentration values for different glass types are reported in Table 2, before and after the flue gas treatment for selenium removal.

In order to compare the concentration levels with the emission limit values applied in most European Countries, a summary of the legislation applied is given in Table 3.

4. Sampling methods for measuring selenium emissions

The measurement of selenium emissions involves a good knowledge of the chemistry that regulates the evaporation of selenium compounds from the glass melt, in order to collect both the particulate and gaseous species that can be present in the flue gas with a ratio that depends on the waste gas temperature.

The sampling train normally consists of a probe, with or without a filter, connected to sampling bottles (2 or 3), containing an absorbing solution. A suitable pump equipped with flow meter, thermometer and vacuum gauge is used to withdraw a sample of the waste gas. A typical sampling train is shown in Figure 3.

Among the laboratories of TC13 members different methods have historically been used to sample selenium emissions, the main differences involve the following aspects:
temperature of the sampling probe;

use and/or position of the filter (inside or out of chimney);
type of absorbing solution;
number of bottles/bubblers;
sampled volume;
washing procedures of the probe and bottles.

A summary of the sampling methods for selenium emissions used by 9 members of the TC13 is given in Table 4. *Note: The laboratories numbered in Table 4 are not necessarily the same as those numbered in the following tables.*

The samples collected with the different methods listed in Table 4 underwent selenium determination by laboratories of TC13 members using suitable analytical procedures discussed below.

5. Analytical procedures for selenium determination

In order to calculate a mass balance of selenium from a glass melting furnace it is necessary to carry out the chemical determination of selenium compounds in of the following samples and materials:

absorbing solution;
particulates collected on filters;
dust from waste gas treatment;
glass.

While the analytical procedure for the determination of selenium can be the same, the preparation of different samples often requires a specific process, in

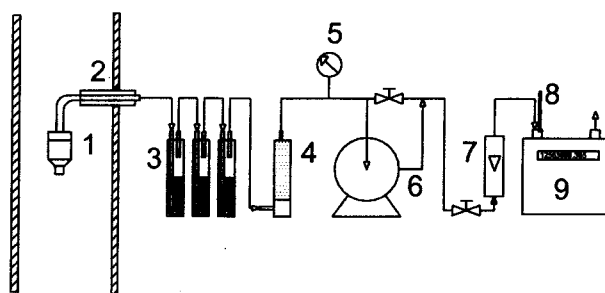


Figure 3. Typical sampling train for selenium emission measurement

- | | | |
|-------------------|----------------|----------------|
| 1 Filter | 4 Silica gel | 7 Flow control |
| 2 Heated probe | 5 Vacuum gauge | 8 Thermometer |
| 3 Washing bottles | 6 Pump | 9 Meter |

Table 4. Summary of historic sampling methods for selenium in waste gases used by TC13 members

Laboratory	Note	Isokinetic	Sample volume (l) & time (min)	Probe	Filter	Absorption train and absorbing solution
1	Note 8	Yes	900 80 min	Heated 160°C glass or titanium	Inside, Quartz fibre	4 bottles with cooling 5% HNO ₃ + 10% H ₂ O ₂
2	Note 1 Note 2	Yes	200-250 40 min	Heated 350°C quartz	None	3 bottles no cooling 1 N HNO ₃
3	Note 3 Note 4	Yes	180 30 min	Heated 350°C quartz or titanium	Inside, Quartz fibre	3 bottles no cooling 0.4 N HNO ₃
4	Note 5 Note 6	Sometimes	180 40 min	Heated 350°C quartz & titanium	Both inside and out, Quartz wool	4 bottles with cooling 0.1 N HNO ₃
5	Note 3 Note 7	No	180-200 40 min	Heated 400°C quartz	Outside	3 bottles no cooling 0.4 N HNO ₃
6		No	400-600 20 min	No heating stainless steel	None	3 bottles 10% HNO ₃
7	Note 10 Note 9	No	180-200 30-40 ?min?	Heated 300°C quartz	Inside, Quartz wool	3 bottles 10% H ₂ O ₂ + NaOH 0.1 N
8	Note 10	Yes	180 120 min	Heated 150°C quartz	Outside, 180°C quartz wool	4 bottles 4.5% HNO ₃ + 1.7% H ₂ O ₂
9	Note 5	Yes	1000 120 min	Heated 150°C glass & titanium	Outside, 150°C quartz fibre	3 bottles 0.1 M HNO ₃

Notes: 1 EPA method for Fluoride; 2 Rinse probes in Br water (sol. 22%); 3 VDI guidelines 3868; 4 Wash probe and connecting parts with Br water; 5 Derived from EPA method but does not cover Se; 6 Br water used, insulate tubing and use small length; so no cooling in connectors; 7 Br water used, do not insulate tubing, but use short length 10-15 cm; 8 Based on method 29 - all glassware pre-soaked in 10% HNO₃ overnight; 9 Wash probe & connecting parts with Br water; and 10 Based on Fr-standard XPX 43051: sampling of heavy metals

order to dissolve the material and eliminate most of the matrix. This is the case for dust and particulate samples and even more so for glass.

Analytical methods widely used for the determination of selenium are:

- x-ray fluorescence (XRF);
- atomic absorption spectrometry (AAS);
- hydride generation atomic absorption spectrometry (HGAAS);
- inductively coupled plasma (ICP-IES);
- neutron activation (INAA).

Some techniques can be applied to any type of sample, but others present limitations. Each method and different sample preparation technique is characterized by a specific detection limit value which can vary significantly.

A comparison of the different analytical techniques was carried out by the ICG-TC13 Selenium Analysis Working Group, using a range of samples:

- (a) glass - flint container and flat bronze;
- (b) dust from a waste gas treatment plant;
- (c) absorbing solution from emission measurements.

5.1 Round robin analysis of selenium in glass samples

To determine the selenium content in two different glass samples a "round robin" analysis was carried out by the laboratories of TC13 members with the results shown in Table 5.

It is clear from the results reported in Table 5 that some analytical methods, in particular the colorimetric method and XRF, are not recommended for the determination of low concentrations of selenium, i.e. below 2-5 ppm Se.

Table 5. Selenium determination in glass - comparison of results

Laboratory	Sample type, and result			Technique
	Float glass sample no. 1 ppm Se	Float glass sample no. 2 ppm Se	Glass container White ppm Se	
A	10.9	10.1	0.8	Polarography
B	9	10	1.5	Colorimetric method
			1.4	XRF
C	10.6	10.7	1.9	XRF
			0.8	HGAAS
D	10.5	9.5	0.85	HGAAS
E	10	12	0.87	HGAAS
F	9	9	1.0	Internal method
G		11.3		Not specified

Laboratory	Sample			Comment	
	Float glass sample no. 1	Float glass sample no. 2	Glass container White		
	Mean value (ppm)	10.0	10.4	1.1	All results
	Standard deviation (ppm)	0.8	1.0	0.4	
	Rel. standard deviation (%)	8.1	10.0	34.7	
	Mean value (ppm)			0.9	Excluding the 1.5, 1.9 ppm values
	Standard deviation (ppm)			0.1	
	Rel. standard deviation (%)			10.4	

Table 6. Selenium determination in absorbing solutions – comparison of results

Sample Laboratory	1a ppm Se	1b ppm Se	2a ppm Se	2b ppm Se	3a ppm Se	3b ppm Se	4a ppm Se	4b ppm Se	Method
A	1.07	0.95	4.38	4.05	8.62	7.73	12.5	11.7	Polarography
B	0.9	1.0	4.7	4.6	8.9	9.0	13.6	13.2	AAS
C	1.5	1.8	5.0	6.1	9.9	10.7	13.8	15.1	AAS
D	1.2	1.3	4.8	5.1	9.0	9.5	13.5	14.1	ICP
E					6.6	8.3	11.0	13.7	AAS
F min	0.9	0.9	4.5	4.6	9.5	9.3	14.1	14.5	ICP
max	1.2	1.4	5.0	5.1	9.7	9.9	14.6	14.5	
G	1.1	1.2	5.0	4.5	8.5	9.5	12.3	13.4	HGAAS
H	1.4	1.4	5.5	5.5	10.3	10.3	14.0	14.6	HGAAS
			4.8	5.2	9.5	10.0	14.1	14.2	AAS
Mean value (ppm)	1.2	1.3	4.9	5.0	9.0	9.4	13.2	13.8	All results
Standard deviation (ppm)	0.2	0.3	0.3	0.6	1.1	0.9	1.1	1.0	
Relative standard deviation (%)	17.9	25.4	6.6	12.8	12.0	10.0	8.2	7.3	

5.2 "Round robin" analysis of selenium in absorbing solutions

In order to compare the analytical methods for the determination of selenium in the absorbing solutions resulting from emission measurements, another "round robin" test was carried out by laboratories of TC13 members. Eight different solutions were prepared for the purpose. These simulated absorbing solutions (1.75% HNO₃) with or without enough sulphuric acid added to investigate the possible interference of absorbed sulphur oxides with the analytical techniques. Four selenium concentrations were assessed, and the solutions were distributed to all the members participating in the comparative analysis:

Sample 1a	1.2 ppm Se + 25 ml HNO ₃
Sample 1b	1.2 ppm Se + 25 ml HNO ₃ + 0.57 ml H ₂ SO ₄
Sample 2a	5.0 ppm Se + 25 ml HNO ₃
Sample 2b	5.0 ppm Se + 25 ml HNO ₃ + 0.57 ml H ₂ SO ₄
Sample 3a	9.5 ppm Se + 25 ml HNO ₃
Sample 3b	9.5 ppm Se + 25 ml HNO ₃ + 0.57 ml H ₂ SO ₄

Table 7. Selenium determination in EP filter dust – comparison of results

Laboratory	Selenium (SeO ₂ %)	Technique
1	1.76	Wet
2	1.67	Wet
3	1.60	Wet
4	1.42	Wet
5	1.63	Wet
6	2.18 *	Not available
7	1.86	Wet
8	1.68	Wet
9	1.83	XRF
10	0.91 *	XRF
11	1.80	Wet
12	1.65	Wet
13	1.3*	XRF
Mean value	1.69	All values excluding those marked by *
Standard deviation	0.13	
Rel. standard deviation (%)	7.7	

Sample 4a	14.0 ppm Se + 25 ml HNO ₃
Sample 4b	14.0 ppm Se + 25 ml HNO ₃ + 0.57 ml H ₂ SO ₄

All the solutions were brought to 1000 ml volume with distilled water. The analytical results obtained by the different laboratories are reported in Table 6.

The data presented in Table 6 show how the same analytical technique can be applied with significantly different results among the participating laboratories. The relative standard deviation values are comparable for both the samples with low and high Se concentrations, indicating a difficulty exists when analysing selenium, even when it is in a "simple" matrix sample such as the absorbing solution used for emission measurements.

5.3 "Round robin" analysis of selenium in a filter dust sample

To complete the assessment of the determination of selenium in all the different materials that are involved in a mass balance calculation, a "round robin" test was carried out by a large number of different laboratories, some being TC13 members, on a sample of filter dust. The results obtained are presented in Table 7, with the indication of the analytical technique applied: wet chemical method or x-ray fluorescence (XRF).

With some exceptions, the results obtained during this round robin test showed a satisfactory relative standard deviation indicating that the laboratories' analysis of such samples was comparable.

6. Parallel measurements of selenium emissions: repeatability and reproducibility tests

Parallel measurements were set up in order to compare different measuring and analytical techniques, normally used by some of the European laboratories that undertake emission measurements. In the first case presented, three different laboratories sampled the waste gases at the same sampling points, before

Table 8. Results of parallel measurements of selenium emissions on a bronze glass melting furnace

	Laboratory A mg/Nm ³ at 8% O ₂	Laboratory B mg/Nm ³ at 8% O ₂	Laboratory C mg/Nm ³ at 8% O ₂
Raw flue gas			
Measurement n. 1	26.0	37.8	18.8
Measurement n. 2	30.6	20.0	27.15
Measurement n. 3	33.2	35.8	19.9
Measurement n. 4	37.1	43.3	29.9
Average value	31.7	34.2	23.9
Calculated value from mass balance	26.2		
	Laboratory A mg/Nm ³ at 8% O ₂	Laboratory B mg/Nm ³ at 8% O ₂	Laboratory C mg/Nm ³ at 8% O ₂
Clean flue gas			
Measurement n. 1	9.72	4.20	6.50
Measurement n. 2	10.5	10.5	7.00
Measurement n. 3	13.3	12.6	10.9
Measurement n. 4	17.5	3.10	12.7
Average value	12.75	7.60	9.28
Calculated value from mass balance	3.2		

and after a waste gas treatment system on a melting furnace producing bronze glass. The results obtained are shown in Table 8.

From the data reported in Table 8 it is evident that selenium measurement is not an easy task to perform; many different factors can influence the final results. It also shows that a mass balance for the calculation of selenium in the waste gas, in particular for estimating the concentration after the treatment system applied to the flue gas is not very accurate. This is discussed below.

It should also be noted that the emission limit value for selenium emissions was exceeded in the case under investigation, showing that removal of selenium from the flue gas is not easy, even when the best available techniques are applied.

An additional parallel measurement has been carried out by two different teams on two furnaces, the first one with high selenium concentration in the flue gas and the second with low levels of selenium. The results are reported in Table 9 and show a very good agreement between the two teams.

In order to test the repeatability of the measurement, a sampling series was performed by a single measuring team on a melting furnace during a four

Table 9. Results of parallel measurement of selenium emissions on two different glass furnaces

	Laboratory 1 mg/Nm ³ at 8% O ₂	Laboratory 2 mg/Nm ³ at 8% O ₂
Furnace A		
Measurement no. 1	9.0	10.6
Measurement no. 2	10.1	11.0
Furnace B		
Measurement no. 1	0.2	0.4
Measurement no. 2	<0.1	<0.1
Measurement no. 3	0.2	0.2
Measurement no. 4	<0.1	<0.1

Table 10. Results of repeatability test for selenium emissions measurements from a glass furnace

Day	Measurement No.	Result (mg/Nm ³)	Average (mg/Nm ³)	Standard deviation
1	1	12.6	11.2	1.33
	2	10.3		
	3	12.4		
	4	9.5		
	5	11.2		
2	1	10.0	10.5	0.36
	2	11.0		
	3	10.5		
	4	10.5		
	5	10.3		
3	1	9.3	10.0	0.65
	2	10.8		
	3	10.3		
	4	10.3		
	5	9.4		
4	1	9.6	9.1	1.12
	2	10.4		
	3	8.7		
	4	7.8		
Total			10.3	1.13

day period, while the operating conditions of the furnace were maintained constant. The results are reported in Table 10.

Investigations concerning the importance of the sampling train used for the measurement of selenium emissions have been carried out in order to determine the amounts of selenium collected in each washing bottle used for the sampling and the criticality of the procedure for washing the sampling line with a suitable collecting solution. The data reported in Table 11 show the results of three different sample runs carried out with conventional washing of the bottles and sampling line using HNO₃.

An additional rinse of the complete sampling line was done using bromine water. Results obtained indicated that a significant amount of selenium, up to 20% of the total, was present inside the line and still had to be recovered.

Table 11. Selenium distribution in washing bottles and sampling line

Sampling No.	1st washing bottle Se mg/Nm ³	2nd washing bottle Se mg/Nm ³	Total in bottles Se mg/Nm ³
1	1.587	0.289	1.876
2	1.318	0.355	1.673
3	1.599	0.148	1.747
Average			1.765
Standard deviation			0.103
Additional washing with bromine water			0.186
Total			1.951
Sampling No.	Total in sampling line Se mg/Nm ³		
1	1.41		
2	1.56		
3	1.89		
Average	1.62		
Standard deviation	0.246		
Additional washing with bromine water	0.67		
Total	2.29		

Table 12. Comparison of measurements of selenium emissions using two different sampling probes (quartz and titanium)

Probe	Temperature (°C)	Filter	Isokinetic conditions	Total Selenium emissions Se mg/Nm ³
Quartz	250	No	No	32.5
Quartz	250	No	No	25.6
Quartz	250	No	No	32.4
Quartz	250	No	No	33.8
Quartz	250	No	No	30.7
Titanium	350	Yes	Yes	32.7
Titanium	350	Yes	Yes	33.9

A comparison between different sampling lines used to measure selenium emissions was carried out by a single operating team using two different measuring procedures:

(a) heated quartz probe at 250°C, without filter and no isokinetic conditions;

(b) heated titanium probe at 350°C, with filter and isokinetic conditions.

The results reported in Table 12 show that the two systems are basically equivalent when all the other conditions are maintained constant (e.g. number of washing bottles, type of rinsing solution, etc.).

7. Mass balance of selenium in a melting glass furnace

A mass balance calculation represents an effective way to determine the suitability of a measuring method for emissions. This approach is not always easy to apply, due to the high number of variables involved in the exercise. A selenium mass balance is not easy to calculate; accurate determination of the selenium in the glass, especially in the case of low concentrations, is particularly difficult.

Two examples of a mass balance are reported, both relate to selenium used as a colouring agent for the production of tinted flat glass. They are presented in Tables 13 and 14.

Comparison of the measured and calculated selenium emissions presented in Table 13 indicates that there is a difference equivalent to 26.5%. The

Table 13. Selenium balance for a tinted flat glass furnace

INPUT (kg/h Se)		OUTPUT (kg/h Se)	
Batch composition	2.08 kg/h	Glass	0.45 kg/h
		Regenerator dust	0.01 kg/h
		Calculated emissions	1.62 kg/h
		Calculated emission concentration	30.6 mg/Nm ³
		Calculated loss of selenium	78.4%

INPUT (kg/h Se)		OUTPUT (kg/h Se)	
Furnace		Float	
Fuel		Oil + natural gas	
Pull		430 ton/day	
Selenium in the melted glass		25 mg/kg (ppm)	
Flue gas volume		53000 Nm ³ /h at 8% O ₂	
Measured selenium emissions		22.5 mg/Nm ³ at 8% O ₂	

Table 14. Selenium balance for a tinted flat glass furnace equipped with flue gas treatment

INPUT (kg/h Se)		OUTPUT (kg/h Se)	
Batch composition	2.56 kg/h	Glass	0.60 kg/h
Cullet	0.15 kg/h	Calculated emissions (raw gas)	2.11 kg/h
		Calculated emission concentration (raw gas)	45.9 mg/Nm ³
		Filter dust (calculated)	2.066 kg/h
		Calculated loss of selenium	77.9%

INPUT (kg/h Se)		OUTPUT (kg/h Se)	
Furnace		Float	
Pull		480 ton/day	
Selenium in the melted glass		30 mg/kg (ppm)	
Flue gas volume		46000 Nm ³ /h at 8% O ₂	
Measured selenium emissions (raw gas)		41.7 mg/Nm ³ at 8% O ₂	(1.92 kg/h Se)
Measured selenium emissions (cleaned gas)		1.0 mg/Nm ³ at 8% O ₂	(0.044 kg/h Se)

measured values were too low. They are nevertheless considered acceptable, considering all the approximations introduced in the balance, as discussed above. Also, in this case the balance did not take into consideration the selenium emitted from the doghouse where an extraction system was installed and equipped with a bag filter. The dust removed from that filter contained 0.34 % of selenium, but the amount per hour was not known.

A better mass balance has been calculated for a float glass furnace equipped with an absorption stage and electrostatic precipitator. The results are presented in Table 14. In this case, the comparison between measured and calculated selenium emissions in the raw gas is relatively good, with a difference of about 9.0%. A balance for the cleaned gas could not be done because the amount of filter dust produced was not known. However, the data shows that a significant amount of selenium should have been found in the filter dust (raw gas emissions minus cleaned gas emissions) and this suggests an exceptionally high selenium absorption rate of 97% occurred.

In both cases presented in Table 13 and 14, the evaporation rate of selenium from the glass melting furnace and its consequent loss was estimated to be about 80%. A similar scenario has been observed in the case of a flint container glass production, where selenium was used as a decolourising agent, showing a final retention in the glass lower than 10%. This is reported in Table 15.

Table 15. Selenium balance for a flint container glass furnace

INPUT (kg/h Se)		OUTPUT (kg/h Se)	
Pull		159 ton/day	
Cullet		48%	
Selenium compound in the batch		ZnSeO ₃	

Selenium INPUT		Selenium OUTPUT	
ZnSeO ₃	97.4%	Glass	7.4%
Cullet	2.6%	Flue gas	92.6%

Historically extremely poor mass balances were calculated in some cases when inappropriate sampling techniques were used, especially those where the sample line was not cooled. The following section describes a recommended sampling method.

8. Recommended sampling method

Based on the information reported earlier in this position paper, a recommended method for the sampling of selenium emissions is proposed. This method takes into consideration the peculiarities of this element, which make some aspects of the measuring procedure particularly critical for achieving a good result.

The proposed sampling method does not differ a great deal from the existing EN 14385:2004 "Determination of the total emission of As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Tl and V"; however, this does not cover selenium.

The principles of the recommended method are the following:

- (a) The sampling probe should be of quartz or titanium.
- (b) A heated probe and line operating at 250°C is preferable, in order to minimise the condensation of selenium along the sampling line.
- (c) The use of a filter is not critical, since most selenium emissions will be present in the flue gas in gaseous form. If a filter is used to separately collect particulate matter, isokinetic sampling conditions are recommended to ensure the accuracy of the measurements.
- (d) A minimum of three washing bottles should be used.
- (e) Nitric acid (HNO₃) is the recommended absorbing solution, with a suggested concentration between 1 and 5%. A combination of nitric acid and hydrogen peroxide (EN 14385:2004) is suitable with a final concentration of 3.3% HNO₃ and 1.5% H₂O₂.
- (f) A complete rinse of the sampling line and washing bottles must be performed at the end of each sample collection period in order to remove selenium condensed along the sampling line. Bromine water must be used for the purpose.

WARNING: Bromine water must be handled with extreme care.

- (g) A minimum waste gas sample volume of 180 l is recommended in order to collect a representative sample for the chemical determination of selenium.
- (h) A minimum sampling time of 30 min is recommended.

9. Conclusions

The reliable measurement of selenium emissions from glass melting tanks requires a good knowledge of selenium chemistry, in order to choose a suitable sampling method and to estimate the concentration in the flue gas. Selenium used for colouring or decolourising the glass has a poor retention rate in the melted glass, normally no more than 10–20%, resulting in high emissions of selenium from the furnace. To comply with the emission limit values for selenium in some European countries, often requires the use of a highly efficient waste gas treatment system for the removal of selenium, when coloured glass or flint container glass are produced. A recommended procedure for sampling selenium emissions from glass melting tanks has been derived. This is based on a thorough understanding of selenium chemistry and several years of observations, measurements and research by members of the TC13.

10. General references

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