VARIABLES IN SOLID PARTICULATE AND FLUORINE MEASUREMENT IN GAS EMISSIONS IN THE CERAMIC INDUSTRY

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ABSTRACT

The present work addressed the study of the influence of different variables on solid particulate and fluorine measurement in gas emissions in the ceramic industry.

The findings were used to determine the most critical factors involved in performing these measurements, and therefore the main sources of possible error. This has enabled proposing certain methods for determining these pollutants, which incorporate a series of simplifications with important savings in time in test performance.

1. INTRODUCTION

The evolution of legislation in virtually all the industrialised nations and the progressive implementation in the companies of environmental management systems (ISO 14000 or the European EMAS regulations), are making it necessary to include environmental controls amongst the manufacturing controls, to assess overall process quality.

In the case of the European Union, most ceramic manufacturing companies will be affected by the application of Directive 96/61/CE on Integrated Pollution Prevention and Control (IPPC), which will require harmonising the enforceable environmental criteria in all the Member States [1].

In ceramic manufacturing processes, air emission control is of great importance to ensuring corporate respect for the environment. The most significant air pollutants in ceramic manufacturing are solid particulates in almost all the production process stages, and fluorine emissions in the firing stages [2].

Present and forthcoming legislation in most EU Member States (Italy, Germany, France, Spain, etc.), as well as voluntary environmental tools (e.g. proposed ceramic tile eco-label), set emission limits for both pollutants and require more frequent emission controls [1].

The main problem in the ceramic industry regarding the performance of these controls is the high number of emission sources (over 10 per company) and test method complexity. Pollutant measurement methods are based on national and international standards and are designed to allow determining pollutants in any facility (e.g. power plants, chemical or ceramic companies). Precisely for this reason, some of the methods are quite complicated, as they are meant to cover every possible situation. Despite this, some of these methods are not wholly appropriate for actual conditions in the ceramic branch.

A study was therefore undertaken to determine the influence of the different variables that affect the determination of solid particulate and fluorine emissions in the ceramic industry, to determine the key variables that are to be accounted for and establish simpler test methods, specifically adapted to the needs of the ceramic industry.

2. MEASUREMENT OF SOLID PARTICLE CONCENTRATIONS IN GAS STREAMS

2.1.- STANDARD METHODS

The standard methods for determining the solid particulates in a gas stream are based on extracting a known volume of this stream, putting it through a particle-retaining filter, weighing the retained quantity, and subsequently calculating the particulate concentration.

The standard methods for determining particulate emissions from fixed sources have been fine-tuned in countries such as Germany and the United States, and though they are not technically identical, they are at least comparable. They basically attempt to establish the necessary conditions to have a representative test stream volume, i.e., containing the same particulate quantity and composition per unit volume as the gas stream to be studied.

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[1] MONFORT, E.; CELADES, I.; MALLOL, G. *Cuestiones sobre medio ambiente para un técnico cerámico.* Castellón (Spain), Instituto de Tecnología Cerámica: AICE, 1999.

[2] MALLOL, G.; MONFORT, E.; BUSANI, G.; et al . *Depuración de los gases de combustión en la industria cerámica.* Castellón: Instituto de Tecnología Cerámica: AICE, 1998.

The main problem involved in getting a representative sample is that the mass of solid particulates is much greater than the molecular mass in the flue gas. This difference increases with the rise in particle size and/or density, so that the hydrodynamic behaviour of the gas and the particulates is different.

For this reason, the different standard methods [3-5] basically establish four conditions for representative sampling, with different degrees of tolerance:

- Isokineticism: The sample shall be taken in such a way that the gas capture rate is equal to the gas velocity in the duct where the entry nozzle is located. To assess the extent to which this condition is met, the ratio of both velocities is calculated, termed the isokineticism factor in this study, represented by I and expressed in %. (Fig.1.1)
- Alignment: The axis of the sampling element (entry nozzle) shall be aligned with the axis of the gas current lines to be sampled. The degree of alignment is measured by the angle between both axes (angle α en Fig.1.2)
- Multiple point sampling: Sampling shall be performed at different points of a gas stream cross section, varying the number of points with sampling area and test method (the number of points per cross section is given by n) (Fig. 1.3).
- Sampling entry nozzle edge design: sampling shall be done with an entry nozzle that distorts gas current lines as little as possible, requiring a simple entry nozzle design with a sharp edge, limiting the maximum angle of this edge (angle β in Fig. 1.4).

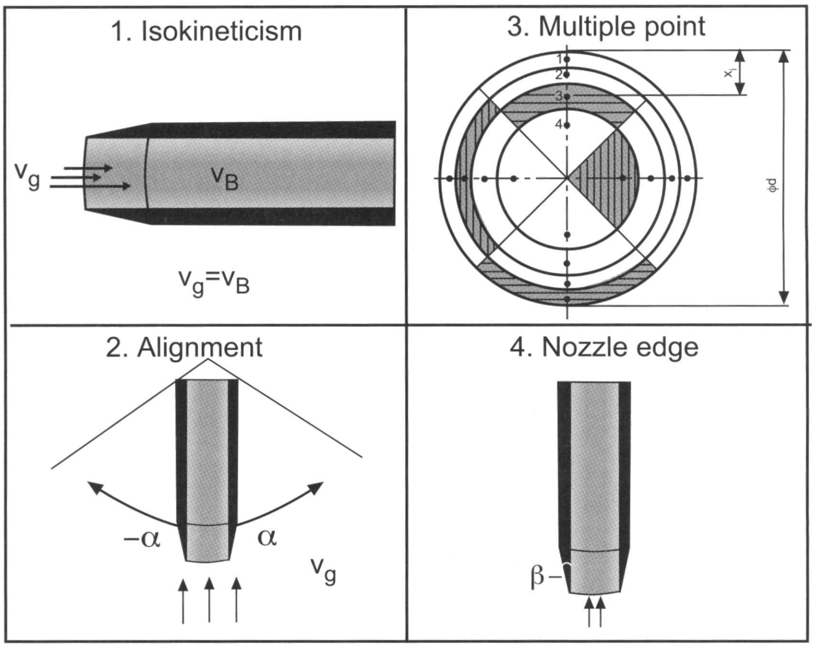

Figure 1. *Main parameters of the test for determining particulate concentration.*

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[3] *Medida y control de emisiones atmosféricas en procesos de combustión.* Octubre 1998. Course organised by the Instituto de Estudios de la energía. C.I.E.M.A.T. Madrid.

[4] ISO 9096. *Stationary source emissions- Determination of concentration and flow rate of particulate material in gas- carrying ducts- Manual gravimetric method.*

[5] UNE 77223. *Determinación de la concentración y caudal másico de material particulado en conductos de gases.*

The test method used in this study for determining solid particulate concentrations in the gas stream is the method proposed in international standard ISO 9096 (recently adopted in Spain as standard UNE 77223) [4-5]. ITC is accredited by the National Accreditation Body (ENAC) for performing this test.

ISO 9096 specifications for these parameters are: I between 90 and 110%, $\beta \leq 20^{\circ}$ and $\alpha \leq \pm 15^{\circ}$. Under these conditions, the solid particulate concentration can be found, according to the standard, with a margin of uncertainty of ± 10%. It has been experimentally confirmed at ITC that this uncertainty value is met, except for particulate concentrations in the stream of less than 20 mg/Nm^3, for which the margin of uncertainty can reach ± 20%.

The sections below study the importance of each of the foregoing variables for measuring particulate concentrations in ceramic industry emissions. The possibility is analysed of simplifying the methodology and/or requirements set out in ISO 9096.

In order to be able to modify some of these variables, part of the study was conducted on a pilot scale, subsequently completing the study with industrial-scale tests.

2.2.- EXPERIMENTAL DEVELOPMENT

2.2.1.- Pilot-scale stage

I) Experimental assembly

The study was conducted using the assembly schematically illustrated in Fig. 2, consisting of the following elements:

- An axial fan and a duct with a circular cross section of 0.4-m diameter, in which mean air circulation speeds are achieved of 10-15 m/s, which are usual values for gas streams in industrial facilities.
- A solid material proportioning system that feeds a preset particulate flow into the air stream.
- Ports for inserting the measuring elements and samplers in the duct, located at a cross section more than 5 diameters from the solids input point and more than 2 diameters from the outlet.

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[3] *Medida y control de emisiones atmosféricas en procesos de combustión.* Octubre 1998. Course organised by the Instituto de Estudios de la energía. C.I.E.M.A.T. Madrid.

[4] ISO 9096. *Stationary source emissions- Determination of concentration and flow rate of particulate material in gas- carrying ducts- Manual gravimetric method.*

[5] UNE 77223. *Determinación de la concentración y caudal másico de material particulado en conductos de gases.*

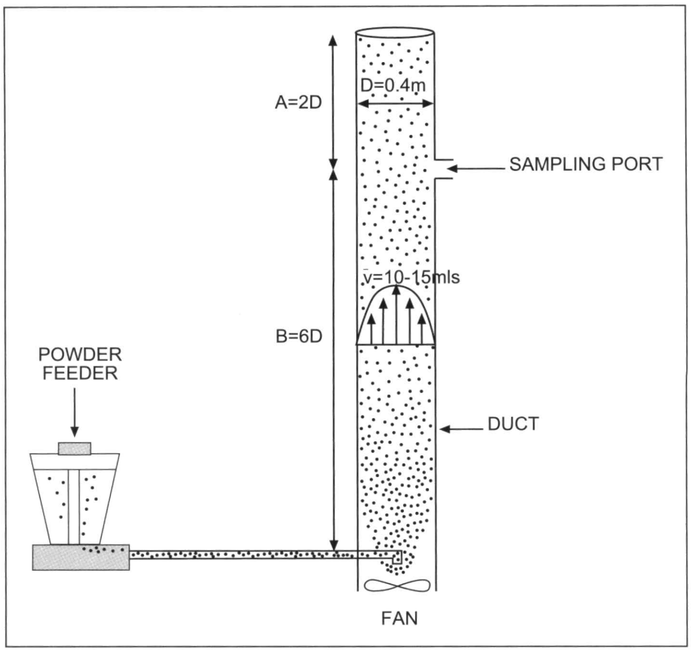

Figure 2. - Pilot stage experimental configuration.

This experimental configuration allowed modifying the type of material input into the air stream, air stream flow rate, and therefore particulate concentration in the gas stream.

II) Material

The material fed into the air stream, which was not changed during the study, exhibited the following characteristics:

- The material used was a standard red-firing clay composition used in the Castellón region for tile manufacture. The clays had been dry milled and contained a 1% addition of fumed silica to raise their flowability and provide constant, appropriate input into the gas stream (consisting of air).
- The material had a density of 2.736 g/cm^3 and a mean diameter of 5.3 μm (measured by a wet method).

A material of the coarsest type (dry milled) was chosen of those commonly found in ceramic industry emissions, therefore with more pronounced inertial effects. The choice was made considering that the possible restrictions found with this material could be extrapolated to practically all the emissions arising in the ceramic branch.

III) Determination of particulate concentrations in the gas stream

The different experiments were conducted as follows:

- All the tests were run by sampling at a single point (duct central point).
- The nominal particulate concentrations were 12, 21 and 50 mg/Nm^3, keeping these concentrations steady with the experimental assembly used within a variation range of ± 10%.

- The following concentrations were determined in each studied condition:

  C_0 : nominal or real concentration, measured under standard conditions, i.e., strictly following the procedure set out in ISO 9096.

  C: measured concentration for the condition being studied, i.e., following the procedure set out in ISO 9096, with the relevant modification.

- The tests were done in triplicate for all the studied conditions, averaging the data.

IV) Studied variables

The variables studied on a pilot scale for each indicated nominal concentration were the isokineticism factor (I), entry nozzle alignment with current lines (angle α) and entry nozzle edge design, modifying the edge angle (angle β).

In the laboratory-scale experiments, the number of sampling points per area (n) was not altered, as the duct in the laboratory set-up was relatively small (0.4 m) and it was considered more interesting to study this variable in larger ducts with possibly more important radial concentration gradients.

2.2.2.- *Industrial-scale study*

The industrial-scale study was performed by selecting emission sources in different process stages at three tile manufacturing companies and two ceramic frit and glaze producers. In all the studied emission sources, the sampling point was located at a position sufficiently far removed from accidents for the sampling cross section velocity profile to meet ISO 9096 requirements [4-5].

With regard to the sampling of particulate solids, the main differences between these emission sources were particulate solids concentration and nature. The nature of the particles determines their behaviour and from this point of view, the ceramic process can be divided into three parts. First, the stages in which the particles consist of body raw materials (composition preparation and pressing). Secondly, stages where the particulates mainly consist of glaze raw materials (glaze preparation and application), and finally particulates generated in the kilns (from tile firing and frit production) [7].

The experiments were conducted following a similar methodology to the one used in the laboratory tests:

- For each studied condition, the concentration was determined under standard conditions C_0 (strictly following the ISO 9096 procedure), and under the condition being studied by C (following the ISO 9096 procedure with the relevant modification).
- The tests were done in triplicate for all the studied conditions, The resulting concentration was expressed as the arithmetic mean of the individual values.

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[4] ISO 9096. *Stationary source emissions- Determination of concentration and flow rate of particulate material in gas- carrying ducts- Manual gravimetric method.*

[5] UNE 77223. *Determinación de la concentración y caudal másico de material particulado en conductos de gases.*

[7] BLASCO, A. et al. *Tratamiento de emisiones gaseosas, efluentes líquidos y residuos sólidos de la industria cerámica.* Castellón. AICE-ITC. 1992.

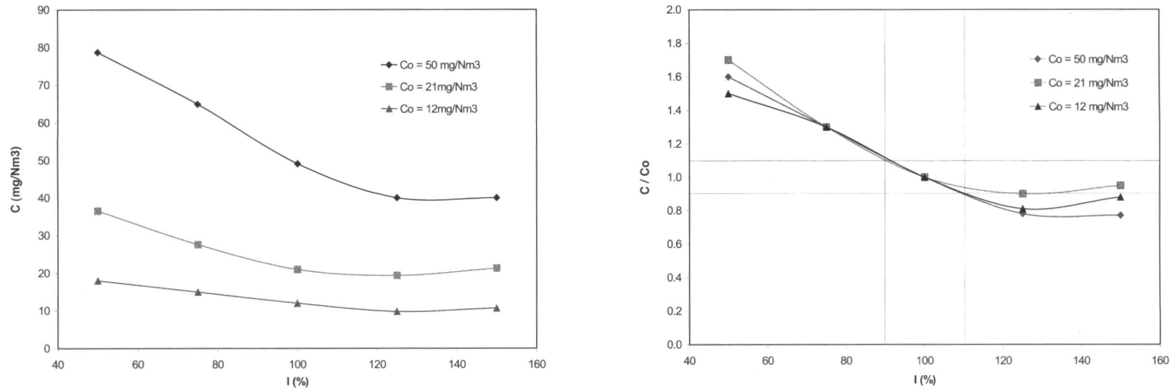
On an industrial scale, the number of sampling points in a gas stream cross section (n) and the isokineticism factor (I) were studied in different emission sources. The series of tests in which the effect of the isokineticism factor was studied were carried out by performing the measurements just at the duct central point.

2.3.- RESULTS AND DISCUSSION

2.3.1.- Laboratory-scale study

I) Influence of the isokineticism factor (I)

Figs. 3 and 4 plot the measured concentration values and the ratio of the measured concentration to the nominal concentration on altering the isokineticism factor.



Figures 3 and 4.- *Influence of the isokineticism factor on particulate concentration measurement.*

The figures show that the measured particulate concentration varies noticeably with the isokineticism factor. The measured concentration dropped with regard to the real concentration when this factor rose (superisokinetic sampling), and the measured concentration rose with regard to the real one when I fell (subisokinetic sampling) as the literature predicts [3].

It can specifically be observed in Fig. 4 that in the studied range the rise in isokineticism (superisokinetic sampling) produced a less pronounced variation in the measured concentration with regard to peak concentration, than when subisokinetic sampling took place. In the case of a nominal concentration of 21 mg/Nm^3 even at isokineticism factors ranging from 125% to 150%, measured concentrations were obtained within the margin of uncertainty allowed by the method (±10%).

The rise in the measured concentration when the isokineticism factor decreases occurs because if gas sample rate at the entry nozzle is lower than duct gas rate, part of the gas stream departs from the initial trajectory and does not enter the nozzle. However, the heaviest particulates, owing to their inertia, do not deviate and enter the nozzle, yielding a sample with a higher particulate concentration than is really the case. This behaviour explains why in the samplings run with a low isokineticism factor, a greater proportion of coarse particles is found on the collecting filters.

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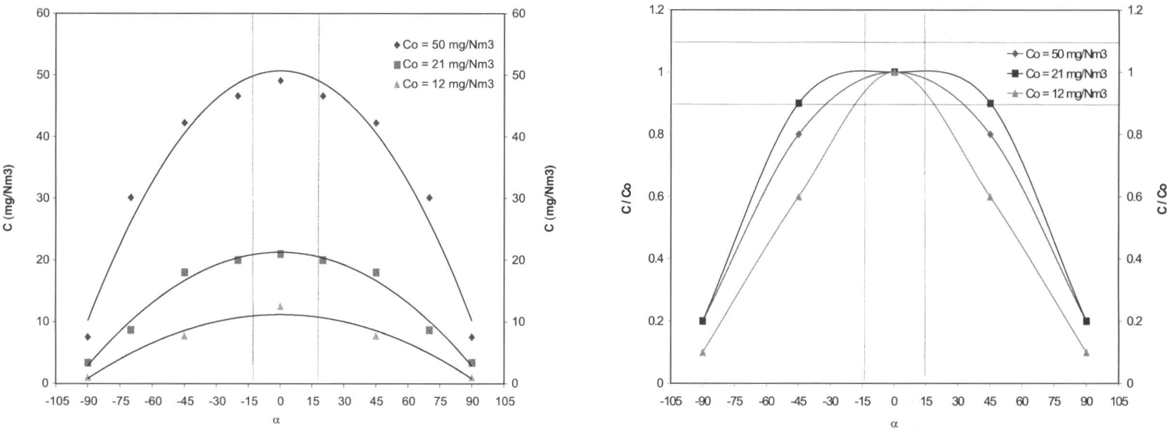
[3] *Medida y control de emisiones atmosféricas en procesos de combustión.* Octubre 1998. Course organised by the Instituto de Estudios de la energía. C.I.E.M.A.T. Madrid.

In the opposite case, when the gas rate in the entry nozzle exceeds that of the gas stream, gas suction occurs from adjacent current lines, which need to depart from their lines to enter the nozzle. However, owing to their greater inertia with regard to the gas molecules, the particles in these stream lines follow their initial trajectory without entering the nozzle and yield a lower particulate concentration measurement than the actual particulate concentration [3].

In accordance with the results, the isokineticism factor is a critical parameter in particle concentration measurement, as set out in the various standard methods. Fig. 4 shows how in the tests conducted, with the exception mentioned above, a variation of factor I exceeding the margin permitted in the standards (±10%) gives rise to errors of over ±10% in the measurement of solid particulates. Therefore, the results obtained indicate the need to respect the ISO 9096 requirement in conducting determinations on ceramic materials, holding the isokineticism factor between 90 and 110%, to ensure the validity of the outcomes.

II) Influence of entry nozzle alignment (α)

Figs. 5 and 6 plot the data obtained on modifying the alignment of the nozzle axis with regard to current lines (angle α).



Figures 5 and 6. *Influence of alignment on particulate concentration measurement.*

The plots clearly show how modifying angle α reduces the measured particle concentration compared to the actual concentration more sharply with lower stream nominal concentration. This is because when the nozzle is sloped in respect of gas current lines, part of the air molecules depart from their trajectory to enter the nozzle. However, the heaviest particles exhibit the greatest inertia and are not captured, producing a more diluted sample.

As in the study of the isokineticism factor, entry nozzle alignment was found to be a critical factor in measuring particle concentration. Fig. 6 shows how a variation of angle α of over 15° produces variations in solid particulate measurements of over 10%. Therefore in this case, the results obtained also indicate the need to meet the requirement set in ISO 9096 of keeping angle α within a range of ±15°, to ensure the validity of the particulate concentration measurement.

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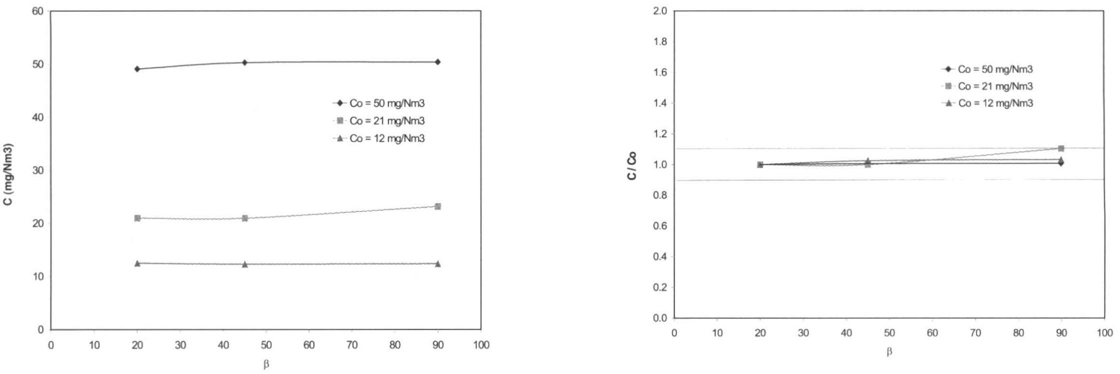
[3] *Medida y control de emisiones atmosféricas en procesos de combustión.* Octubre 1998. Course organised by the Instituto de Estudios de la energía. C.I.E.M.A.T. Madrid.

III) Variation of entry nozzle edge angle (β)

To conduct this test, entry nozzle design was modified. The tests were run with entry nozzles having edge angles of 20 (maximum permitted ISO 9096 angle), 45 and 90°. In every case, entry nozzle wall thickness was kept in the range 0.1-0.2 mm.



Figures 7 and 8. *Influence of entry nozzle edge angle (β) on particle concentration measurement.*

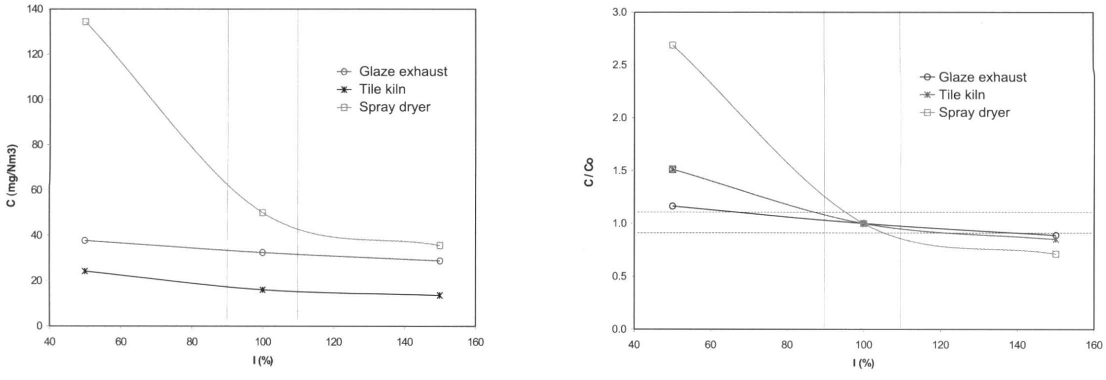
Figs. 7 and 8 show how under the studied conditions, the variation of angle (of the entry nozzle hardly affected measured particle concentration. Consequently, for gas streams with particles of a similar nature, and a wall thickness of the order indicated, the nozzle sharpness angle is a factor that does not significantly affect the measured solid particulate concentration in the gas stream. These findings indicate the possibility of using entry nozzles in the ceramic industry with greater sharpness angles than laid down in ISO 9096, which are therefore mechanically more robust, for determining gas stream particle concentrations.

2.3.2.- Industrial-scale study

I) Variation of the isokineticism factor (I)

The study of the influence of the isokineticism factor developed on a laboratory scale was rounded off with industrial tests. Three emission sources were chosen of solid particulates of differing nature: spray dryer, glaze preparation and application section exhausting system, and ceramic tile firing kilns.

Figs. 9 and 10 plot the industrial-scale data. In the calculation of the C/C_o quotient, the mean concentration of the values found for factor I of 100% was used as the value of C_o.



Figures 9 and 10. *Variation of concentration with regard to the isokineticism factor.*

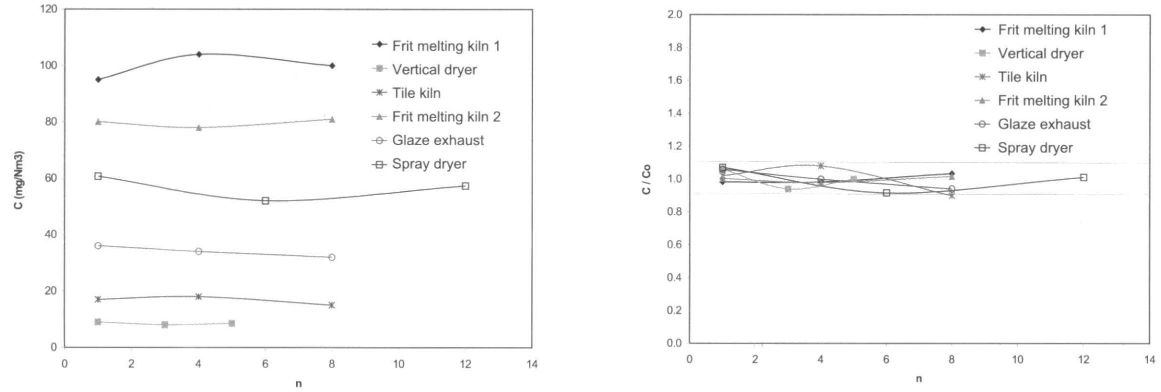
The industrial-scale data presented in Figs. 9 and 10 are similar to those found on a laboratory scale, with the measured concentration being altered when the isokineticism factor changed. It was similarly found that the departure from the measured concentration with regard to the actual concentration was more pronounced when sampling was performed at low isokineticism factors. Thus, at all the studied sources, it was observed that sampling should be conducted isokinetically to ensure data reliability.

II) Variation of the number of points per cross section (n)

As indicated above, the various standard methods establish the need to extract samples at different points in a gas stream cross section to obtain a representative sample. The number of points varies with cross-sectional area and the applied standard method.

To verify the influence of this variable on particle concentration, particulate concentration measurements were performed at different ceramic company emission sources, following the procedure set out in ISO 9096, and reducing the number of sampling points required by this standard.

Figs. 11 and 12 plot the data obtained, taking the mean concentration found in each case as the nominal gas stream concentration.



Figures 11 and 12. *Variation of concentration with the number of sampling points.*

In accordance with the findings at the studied industrial facilities, the number of sampling points per cross section has no significant effect on the value of the measured particulate concentration. This means that in the studied streams, there were no noticeable particulate concentration radial gradients, as the determination of the particulate concentration by extracting samples at a single (central) point gave an equivalent value to sampling at different points in the cross section.

The explanation for this behaviour could be that in every case, a turbulent gas circulation regime was involved. Thus, the samples were taken in stacks with a circular cross section and diameters ranging from 0.5 to 2m, at mean gas stream rates of between 10 and 20 m/s. Under these conditions, the Reynolds modulus is larger than 10^4 so that the circulation regime is turbulent and owing to the density and morphology of the solid particles contained in these streams, a homogeneous particle mixture is produced in the gas stream.

If the various emission sources are compared, they can all be observed to exhibit similar behaviour, even the fritting kilns. However, the fritting kilns constitute a special case, as the nature (particle density and size) and origin (drawn off raw materials or particles formed by condensing volatiles in the kiln) of the solid particulates in the emissions can be highly variable [2]. An in-depth study of the behaviour of the particulates found in frit melting kilns is very complex, and the results obtained should be rounded off with a specific study.

These results are of considerable interest from a practical point of view, as the simplification involved of being able to extract a sample at a single point in the stack cross section facilitates testing while providing considerable savings in time (in certain cases up to 30%).

3. FLUORINE CONCENTRATION MEASUREMENT IN GAS EMISSIONS

Fluorine compounds are basically found in ceramic industry emissions as gaseous compounds in the firing stage. In general, the fluorine in the kilns used for firing ceramic materials arises as a result of clay mineral decomposition above temperatures of around 500-600°C. The major compounds that form are hydrofluoric acid, silicon tetrafluoride, and to a lesser extent alkali fluorides as particles, these last compounds being virtually negligible [2] [6-7]. In this study, as in the literature, these substances are termed fluorine compounds or simply fluorine emissions, though in reality, a series of substances is involved containing this element.

In ceramic tile kiln emissions (or those of similar ceramic products), the relatively small presence of solid particulates, which contain a minor quantity of fluorine in their composition, explains why the literature [2] [6] [8] considers the fluorine released as solid particles to be negligible compared to the gaseous compounds. The present study has therefore focussed on determining the fluorine compounds released in the gaseous phase.

3.1.- STANDARD METHODS.

The standard methods currently used for determining fluorine compounds in the gaseous phase are based on extraction by means of a suitable probe with a known gas volume, making it pass through an absorption system that captures these compounds. The fluorine contained in the captured solution is then determined and the concentration in the gas stream calculated.

Various standard methods have been advanced in the literature for determining fluorine compounds in gaseous emissions, which define a series of necessary requirements for the test to develop appropriately [6][9-11]. The important features in this test are:

- Materials used to make the probe tube and probe temperature. A given type of material is recommended depending on the standard consulted, the most common being quartz, Teflon, stainless steel or borosilicate glass. The material shall not

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[2] MALLOL, G.; MONFORT, E.; BUSANI, G.; et al . *Depuración de los gases de combustión en la industria cerámica.* Castellón: Instituto de Tecnología Cerámica: AICE, 1998.

[6] MAZZALI, P.; *L'Inquinamento atmosferico. Origine, prevenzione y controllo.* Bolonia. Ed. Pitagora. 1989.

[7] BLASCO, A. et al. *Tratamiento de emisiones gaseosas, efluentes líquidos y residuos sólidos de la industria cerámica.* Castellón. AICE-ITC. 1992.

[8] GAZULLA. M.F.; GÓMEZ, M.P.; CABRERA, M.J.; MONFORT, E. *Determinación de flúor en las arcillas utilizadas en la fabricación de baldosas cerámicas.* Técnica Cerámica, 243, 298-302, 1996.

[9] EPA, MÉTODO 13B. *Norma característica para la determinación de flúor.*

[11] UNICHIM 580 *Misure alle emissioni. Flussi gassosi convogliati. Determinazione dei fluoruri gassosi e dei fluoruri particellari. Metodo potenziometrico.*

react with the fluorine in the studied gas stream. Probe tubes with and without heating can be used. However, if the tube is not heated, possible condensations need to be controlled.

- Absorption system. With regard to the absorbing reagents in the bubblers, the most widespread absorbing reagent is a sodium hydroxide solution. On the other hand, the variables that change from standard to standard are the number and design of the absorption units (bubblers).
- Exhausted gas volume flow rate. The standards usually establish a maximum flow rate to assure high fluorine compound capture output. When solid particles and fluorine compounds are to be captured, sampling shall be performed under isokinetic conditions, respecting the indicated maximum flow rate.
- Sampled gas volume. A minimum gas sample volume is usually established to obtain a measurable quantity of fluorine in the absorbing liquid with the analysis technique used. This volume obviously varies with gas fluorine compound concentration.
- Fluorine analysis in an absorbing reagent. The analysis technique used in determining fluorine compounds in the absorbing reagent shall be specific and accurate, i.e., sensitive and free of interference from other substances. The most common fluorine determination technique found in the standards is the potentiometric method with a fluorine ion-selective electrode.

In this study, a test procedure fine tuned at ITC was used to capture fluorine compounds, based on U.S. and Italian standards [2] [6] [9-10]. The sampling train and test conditions are described below:

- The probe tube metal and the glass elements were lined with Teflon to avoid reactions with the fluorine. It was verified beforehand that the type of Teflon used did not absorb or release fluorine compounds under the test conditions.
- A non-heated probe tube was used.
- The absorption system consists of two bubblers containing NaOH 0.1 N, a third empty bubbler and a fourth one with silica gel.
- Sampling need not be performed under isokinetic conditions, as the fluorine compounds are found in the gaseous phase.
- The exhaust gas flow rate is kept constant with values of around 5 l/min.
- Exhaust gas volume was around 200 litres.
- The potentiometric method was used to analyse the fluorine in the capturing solution with the fluorine ion-selective electrode according to the ASTM D1179 standard.

Under these operating conditions it was found at ITC that for hydrofluoric acid concentrations of the order of 10 to 50 mg/Nm^3, usual values for ceramic production kiln

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[2] MALLOL, G.; MONFORT, E.; BUSANI, G.; et al . *Depuración de los gases de combustión en la industria cerámica.* Castellón: Instituto de Tecnología Cerámica: AICE, 1998.

[6] MAZZALI, P.; *L'Inquinamento atmosferico. Origine, prevenzione y controllo.* Bolonia. Ed. Pitagora. 1989.

[9] EPA, MÉTODO 13B. *Norma característica para la determinación de flúor.*

[11] UNICHIM 580 *Misure alle emissioni. Flussi gassosi convogliati. Determinazione dei fluoruri gassosi e dei fluoruri particellari. Metodo potenziometrico.*

[10] VDI 2470. *Measurement of gaseous fluorine compounds* (1975).

emissions, the concentration had a margin of uncertainty ± 15%. This variability is of the order established in the literature [12].

3.2.- MATERIALS AND EXPERIMENTAL PROCEDURE

3.2.1.- Laboratory-scale study.

Figure 13 schematically illustrates the configuration designed for the laboratory-scale study, consisting of:

- A bottle of reference gas with a known concentration of hydrofluoric acid.
- A gas volume flow rate regulation system (pressure reducer).
- A sampling train consisting of a probe tube and an absorption unit with four bubblers.
- A sampled gas volume control unit.

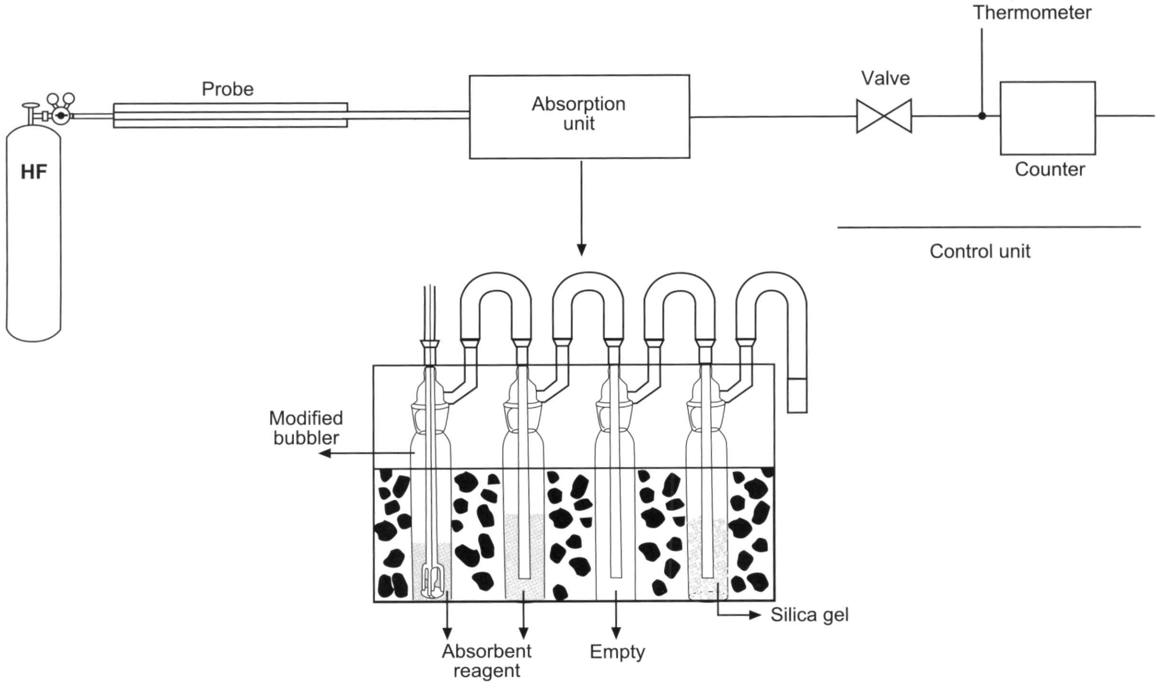

Figure 13. *Schematic illustration of the laboratory assembly used to study fluorine capture.*

The experimental set-up enables starting with a gas of known HF concentration, modifying this concentration (using different standard blanks), varying the flow rate and/or exhaust gas volume, and obviously the sampling train configuration.

The reference bottle used in this study had an HF concentration of 22±3 mg/Nm^3 with nitrogen as carrier gas (concentration C_o in the laboratory tests).

The laboratory experiments were conducted in the following order:

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[12] *Methods for measuring chlorides and fluorides in waste gas emissions from glass melting tanks.* Technical Committee 13, Pollution, of the International Commission on Glass. Glass Technology Vol. 31 nº 4, August 1990.

- During a period of time of not less than 5 minutes, the gas mixture from the bottle was circulated through the circuit, bypassing the absorption unit. The purpose of this operation was to ensure gas venting in the circuit and passivation of the possible elements that might react with HF.
- Sampling
- Collecting the capturing solution and circuit washing liquid.
- Determination of the fluorine concentration in the resulting capturing solution by preparing the corresponding calibration curve and validating this for each series of experiments.
- All the series of experiments were triplicated. The resulting concentration was expressed as the arithmetic mean of the individual values.

The following variables were studied in the laboratory experiments:

- The material of which the probe tube was built, from the gas exit from the blank until it enters the absorbing solution.
- The nature and concentration of the absorbing solution contained in the bubblers.
- Sampled gas volume flow rate.
- Sampled gas total volume.

The relative importance was also studied of the liquid obtained on washing the circuit.

3.2.2.- Industrial-scale study

To complete the study, sampling was done at tile firing kilns located in ceramic tile manufacturing companies, following the test procedure set out above.

The main differences with the laboratory-scale samplings were flue gas temperature (between 150-220°C), gas moisture content (5-10 vol%) and the presence of other pollutants that could produce interference (HCl, CO, etc.). [2].

The tests were carried out with a methodology similar to the one adopted in the industrial tests for determining solid particulates:

- Determination in each studied condition of:

  C_o: nominal or actual concentration, determined by the standard procedure (point 3.2.1.).
  C: measured concentration in the test condition, i.e., following the procedure indicated (point 3.2.1.), however with the relevant modification.

- A series of three experiments was performed in each studied condition. The arithmetic mean of the individual values yielded the resulting concentration.

The variables studied on an industrial scale were the sampling train material, and

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[2] MALLOL, G.; MONFORT, E.; BUSANI, G.; et al . *Depuración de los gases de combustión en la industria cerámica.* Castellón: Instituto de Tecnología Cerámica: AICE, 1998.

the exhaust gas volume flow rate. The quantity of fluorine compounds retained in the circuit washing liquids was also evaluated.

3.3.- RESULTS AND DISCUSSION

3.3.1.- Laboratory-scale study

I) Influence of sampling train materials

In this part the influence was studied of the material of which the sampling probe tube was built, eventually determining whether it was necessary to take any type of measure to avoid reactions of the gas stream with sampling train material.

The sampling train set out in point 3.2.1 was set up for this purpose, varying the nature of the circuit material in touch with the studied gas stream, from the point the gas exited the bottle until it entered the absorbing solution.

In the first place, a Teflon-lined material was used, according to the proposed method, with a stainless steel probe tube, and glass and polyethylene bubblers. Table 1 sets out the results.

SERIES	PROBE MATERIAL	BUBBLER MATERIAL	C (mg HF/Nm^3)
1	Teflon	Teflon-lined glass	19.8
2	Teflon	Polyethylene	19.5
3	Teflon	Glass	24.7
4	Stainless steel	Glass	1.4
5	Stainless steel	Teflon-lined glass	7.0

Table 1.- *Influence of sampling train materials.*

The probe tube material can be observed to noticeably affect the final sampling result. Under the studied test conditions, the stainless steel of the probe is basically the material that reacts with the fluorine in the gas stream, yielding a value that was much lower than the actual value. Thus, the use of sampling trains such as those of series 4 and 5 lead to serious errors in fluorine determination.

II) Influence of the nature and concentration of the absorbing reagent in the bubblers

In this case, based on the reference standards [9-12], tests were conducted by modifying the nature of the absorbing liquid and the NaOH concentration. The volume of the capturing solutions was held steady. The results obtained in these samplings are given in Table 2.

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[9] EPA, MÉTODO 13B. *Norma característica para la determinación de flúor.*

[11] UNICHIM 580 *Misure alle emissioni. Flussi gassosi convogliati. Determinazione dei fluoruri gassosi e dei fluoruri particellari. Metodo potenziometrico.*

[12] *Methods for measuring chlorides and fluorides in waste gas emissions from glass melting tanks.* Technical Committee 13, Pollution, of the International Commission on Glass. Glass Technology Vol. 31 nº 4, August 1990.

SERIES	ABSORBING REAGENT	CONCENTRATION	C (mg HF/Nm^3)
6	NaOH	0.10 N	21.5
7	NaOH	0.01 N	22.7
8	KOH	0.05 N	23.4

Table 2. *Influence of the nature of the absorbing solution on the fluorine determination.*

In this case, there were no substantial variations in the findings, so that using KOH is feasible as an alternative solution to sodium hydroxide for capturing HF, as proposed in certain standards [9,10] [12]. Similarly, the use of solutions with variable NaOH concentrations (series 6 and 7) had no effect on the findings.

In all the conditions, precaution must be taken to have an excess quantity of absorbent with regard to the amount of retained fluorine.

III) Influence of gas volume flow rate and sampled total volume

In this part, different samplings were performed, first varying the exhaust flow rate and holding the exhaust gas volume and then varying the sampled total volume for a constant flow rate. Table 3 sets out the results.

SERIES	EXHAUST FLOW RATE (l/min.)	SAMPLE VOLUME (l)	C (mg HF/Nm^3)
9	3	200	21.5
10	5	200	23.1
11	10	200	21.3
12	30	200	23.9
13	5	45	18.5
14	5	150	23.0
15	5	200	24.4
16	5	300	22.8

Table 3. *Influence of exhaust flow rate and sample volume in the HF determination..*

In this series of tests it can be observed that at least up to flow rates of 30 l/min, modifying the exhaust flow rate had a negligible effect on the HF determination. On modifying the sample volume, all the values were found in an acceptable range, although the result found in test series no. 13, with a sample volume of only 45 litres, lay slightly below the admissible lower limit, so that the minimum sample volume to be captured will lie at around 150 litres.

It should be remembered that these values were obtained with a bottle that had a homogeneous HF concentration, whereas on an industrial scale, gas fluorine concentration can vary with time. However, from a practical point of view, these results are of considerable interest, as they allow reducing the time required to run the tests, using volume flow rates of up to 30 litres/min and capturing volumes of the order of 200 litres, at least when working with emissions that can be considered continuous and constant, as is the case with tile-manufacturing kilns under given operating conditions (same size, same model, items with the same residual moisture content, etc.).

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[9] EPA, MÉTODO 13B. *Norma característica para la determinación de flúor.*

[10] VDI 2470. *Measurement of gaseous fluorine compounds* (1975).

[12] *Methods for measuring chlorides and fluorides in waste gas emissions from glass melting tanks.* Technical Committee 13, Pollution, of the International Commission on Glass. Glass Technology Vol. 31 nº 4, August 1990.

3.3.2.- Industrial-scale study

To round off the study, certain laboratory-scale results were verified on an industrial scale. Table 4 presents the results obtained on varying the gas exhaust rate and sampling train material.

SERIES	PROBE TUBE MATERIAL	BUBBLER MATERIAL	EXHAUST FLOW RATE (l/min)	C (mg HF/Nm^3)
17	Teflon	Teflon-lined glass	5	19.6
18	Teflon	Teflon-lined glass	20	22.3
19	Stainless steel	Glass	5	4.0

Table 4. *Industrial tests varying the sampling train and exhaust flow rate.*

Table 4 shows that the industrial-scale data are analogous to the laboratory-scale data. That is, gas exhaust flow rate in the studied range of values is not a significant factor, while the type of materials making up the sampling train is a critical factor in determining fluorine in kiln emissions.

3.3.3.- Importance of sampling train washing liquids

Finally, in two series of laboratory and industrial tests the retained fluorine was analysed separately in the sampling washing train and in the bubblers, to determine the relative importance of each. Table 5 reports the data, showing the measured fluorine compound concentrations in the analysed streams (C_o).

SERIES	CONDITIONS	WASHING LIQUIDS	FIRST BUBBLER SOLUTION	SECOND BUBBLER SOLUTION
20	Laboratory: C_o=22 mg/Nm^3	1	99	<1
21	Industrial: C_o=20-40 mg/Nm^3	30	70	<1

Table 5. *Fluorine retained in the different solutions obtained in sampling (% in respect of total fluorine).*

In the industrial data, the importance can be observed of the circuit washing operation, as the fluorine collected in the solution is about 30% of the total fluorine. In the series of laboratory-scale experiments, fluorine capture from the washing liquids was virtually negligible. These very important differences essentially lie in the fact that in the industrial tests, kiln exhaust gases have very high temperatures and a moisture content of about 5-10% (by volume). Therefore, when a non-heated probe tube is used, part of this vapour condenses and retains fluorine compounds by absorption, while in the laboratory experiments, the gaseous mixture is at ambient temperature and practically free of water vapour.

These findings indicate that in sampling hot emissions containing water vapour, at least when working with non-heated probe tubes, a suitable sampling train washing method is required, while using materials that do not react with the fluorine compounds in the gas and liquid phase. Studies were found in the literature [6,12] confirming that when non-heated, stainless steel probe tubes are used, the arising condensates react with the tube, giving rise to significant errors in the fluorine determination in the gas stream.

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[6] MAZZALI, P.; *L'Inquinamento atmosferico. Origine, prevenzione y controllo.* Bolonia. Ed. Pitagora. 1989.

[12] *Methods for measuring chlorides and fluorides in waste gas emissions from glass melting tanks.* Technical Committee 13, Pollution, of the International Commission on Glass. Glass Technology Vol. 31 nº 4, August 1990.

4. CONCLUSIONS

- A pilot-scale configuration was designed and fine-tuned for producing gaseous streams with suspended particles, simulating the streams produced in the ceramic industry. In this assembly, solid particulate composition and concentration, gas flow rate and the different sampling variables can be modified.
- In both the laboratory and industrial tests run to determine the solid particulate concentration in ceramic industry emissions, the most critical factors were found to be the isokineticism factor and the alignment of the entry nozzle with the current lines. Instead, the entry nozzle edge angle and number of sampling points in a cross-sectional area of the stream did not have a very significant effect on solid particulate concentration measurement.
- The outcomes are of great practical interest as they allow conducting solid particulate measurements at a single sampling point per cross section, which, with the constraints mentioned in the text, enable simplifying the test and saving up to 30% of the time required to perform the test.
- A very simple laboratory assembly has been designed and fine-tuned for measuring gas emission fluorine compound concentrations, which allows studying the influence of the different variables using a gas with a known composition.
- It was found in the pilot-scale and industrial experimentation that the most critical factor in the determination of fluorine compounds is the material used to build the sampling train. When a water-vapour containing, high-temperature gas stream is involved, and sampling is done with a non-heated probe tube, the presence of sampling train washing liquids is also a critical factor. However, within certain reasonable margins, exhaust gas flow rate and total sample volume had no significant effect on determining fluorine compound concentration.
- From a practical point of view, the findings indicate the possibility of reducing fluorine sampling time using relatively high exhaust rates as long as continuous, constant emissions are involved.

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