APPLICATION OF AN ON-LINE MEASUREMENT SYSTEM FOR HF EMISSION CONTROL

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ABSTRACT

The present study describes the adaptation of an on-line HF analyser in real time, based on laser technology, for control of emissions from ceramic tile manufacturing kilns.

The operation of the equipment was verified in several industrial facilities. The verification method consisted of comparing the on-line measuring system data with the results obtained in batch gas samplings (chemical method). For the batch determination of the fluorine concentration, an internal method developed by the Instituto de Tecnología Cerámica (hereafter ITC), based on standard methods, has been used. ITC is accredited by the Spanish National Accreditation Body (ENAC) for the performance of this type of sampling.

The on-line HF measurement system has been used to study the behaviour of HF emissions in standard ceramic tile firing kiln operating conditions and on implementing different actions in these kilns.

Keywords: *Environment, atmospheric emission, HF, firing of ceramic tiles.*

1. INTRODUCTION

The growing concern for issues relating to the protection of atmospheric pollution and the application of increasingly stringent regulations in this regard require companies to have tools in place for fast and simple on-line control of their emissions. At the same time, these systems also enable demonstrating conformity to regulatory emission limits, as well as determining how any modification of the process affects the emissions.

Currently, one of the global regulatory tendencies in environmental issues is the protection and control of the environment as a whole, i.e., in an integrated way. A clear example of this is the approval of Directive 96/61/EC on integrated pollution prevention and control (IPPC). This is considered to be the most important European regulation on the industrial environment in recent years and forms the basis for the environmental regulations in each EU Member State (transposed to Spanish legislation by means of Law 16/2002).

One of the new features that this Directive introduces is the endeavour for informative transparency, by making public the content of authorisations, emission inventories, etc. A series of instruments has been developed for this purpose, such as the European Pollutant Emissions Register (EPER). This tendency to foster environmental informative transparency is due to a greater social awareness regarding these subjects, and requires the Administration to inform citizen about the environmental situation.

The need to respond to this requirement and others introduced by the entry into force of the IPPC Directive significantly affects all the sectoral industrial facilities envisaged in Annex I of the Directive. The Spanish ceramic industry is one such industrial sector listed in Annex I of the IPPC Directive[1].

In accordance with these regulations, pollutant emission limit values are established based on the Best Available Techniques, which are set out in the so-called sectoral BREFs (Best Available Techniques Reference Documents). Although the BREF applicable to the ceramic industry has not yet been approved, a review of existing regulations and sources of emission value data makes it clear that control of fluorine compound emissions in the firing stage will be one of the key issues to be addressed in the BREF devoted to minimising the environmental impact of this industrial activity[2].

Fluorine compounds are essentially present in ceramic industry emissions as gaseous compounds. For this reason, fluorine emissions in the form of solid particles, at least in the ceramic tile industry, can be considered negligible compared with gaseous compounds.

The standard methods currently used for measuring fluorine compounds in gaseous emission are based on extraction with an appropriate probe of a known volume of gases. The gas volume is then put through a solution that captures the fluorine compounds by absorption, followed by chemical analysis, thus enabling the fluorine concentration in the emission to be calculated[3-4].

These standard methods have a high accuracy, if the due precautions are taken[5], but they display serious disadvantages when it comes to industrial facilities. The drawbacks include a relatively long time (sampling time and subsequent sample analysis) to obtain a mean result of the sampling period. This is why it does not have a high control frequency and is therefore an unsuitable method for continuous monitoring of the emissions.

For the foregoing reasons, it was considered of interest to perform a search for on-line measurement methods. This has led to the present study by ITC in collaboration with Boreal Laser Limited and the Department of Electrical Engineering of the University of Alberta (Canada) aimed at adapting a system based on laser technology for on-line control of fluorine stack emissions in the ceramic industry.

The objectives of the study were:

- Definition of an equipment configuration adapted to the characteristics of ceramic industry facilities and emissions.
- Validation of the data obtained with the laser equipment by comparison with those obtained by the standard chemical method.
- On-line monitoring of the fluorine emissions at industrial facilities under different operating conditions to evaluate the response capacity of the equipment.

2. MEASUREMENT OF FLUORINE COMPOUNDS IN GASES

2.1. ON-LINE GAS MEASUREMENT METHODS

The on-line measurement of a pollutant enables systematic monitoring of its variations in an emission or discharge. Having on-line measurements is of great interest, since this allows observing possible variations in the emission with time, and studying their relation to manufacturing process and/or emission treatment variables, thus providing information for appropriate decision-taking and correct eco-management, for instance by optimising emission treatment systems.

On-line gas measurement methods in gaseous streams can basically be divided into two groups:

- **Extractive methods:** These are based on extracting a representative sample of the gas, and running it through a detection and/or analysis system, typically to determine gas concentrations based on optical methods, conductivity measurement, analysis by selective electrodes, etc. In the fluorine determination in the ceramic industry at least two instruments of this type are found in the literature. In one of these, the sample is absorbed in a solution and the concentration is determined by means of a selective electrode. This is done by extracting gas with a certain frequency, which provides good monitoring of the evolution of the fluorine concentration with time[6]. The other instrument is based on laser technology, and has been used in previous studies conducted by ITC in co-operation with emission treatment equipment producers for continuous monitoring of fluorine emissions in the ceramic industry[7]. The main difficulty encountered with emission extractive equipment is that the concentration of the element of interest, in this case fluorine, shall not be modified in the sampling line or the conditioning system, by undesired reactions, sample losses or uncontrolled dilutions, etc. Such effects can cause the gas sample that reaches the analyser to have a different composition from that which it had in the stack. This is particularly critical for reactive gases such as HF, NH_3 and HCl.

- **In situ measurement methods:** The most widespread methods of this kind are optical methods, which are based on sending radiation through the gaseous stream and determining the transformation that the signal undergoes on its course. Optical absorption methods are based on determining the attenuation of a radiation of different nature. In terms of type of radiation and technology used, these methods basically work with ultraviolet radiation (UV), infrared radiation (IR or FTIR) and laser systems. The main advantage of these non-extractive methods is obviously avoiding the problem of disturbing the sample, while a continuous signal is obtained in real time. The principal problem with these methods is the requirement for high specificity and appropriate detection limits.

2.2. ON-LINE MEASUREMENT SYSTEM REQUIREMENTS: SELECTION REQUIREMENTS

In order to select a fluorine compound measuring system adapted to the needs of the ceramic tile industry the following system requirements were established:

- **Specificity and sensitivity:** If natural gas is used as fuel, in addition to fluorine the following combustion gases are found in ceramic tile kilns: H_2O (5-10 vol%), CO_2 (1-4 vol%), CO (1-100 mg/Nm^3), HCl (20-150 mg/Nm$_3$), SO_2 (1-200 mg/Nm^3) and solid particulates (< 15 mg/Nm^3). Therefore, HF must not be influenced by the presence of these compounds. On the other hand, the fluorine concentration in this stream is relatively low (normally below 50 mg/Nm^3) as are the legal emission limits (of the order of 5 mg/Nm^3), so that low detection limits are required.
- **Portability:** As companies in the ceramic tile industry have several kilns and these are sometimes located quite far from each other, sometimes even in different plants, having portable instruments with relatively short assembly and disassembly times is considered essential.
- **Temperature:** An important parameter is emission temperature, which is of the order of 150 to 250°C. Therefore, the elements in contact with the stack must be able to withstand these temperatures. In addition, the control unit must be able to run at ambient temperatures that can reach 40°C.
- **Calibration:** Another key factor in the selection of an on-line system is the calibration methodology, since some instruments have a complex calibration procedure that actually limits much of their usefulness.

Consequently, after studying various in situ instruments and measurement systems, it was decided to adapt a commercially available instrument to develop a configuration that met these requirement criteria.

2.3. ON-LINE MEASUREMENT WITH A LASER SYSTEM

Diode laser-based gas detectors, known as tuneable diode lasers (TDL), are being increasingly used in environmental applications for safety, air quality and on-line monitoring of industrial processes.

Systems with infrared spectrometry coupled with tuned lasers work on a single pre-set wavelength. At ambient temperature they emit near infrared (NIR) radiation. Many gases of environmental interest (CO, NO, HF, HCl, etc.) absorb NIR radiation and each gas has a unique absorption spectrum. A TDL selects a single absorption band of a given gas, which displays no interferences with any other gas. This makes these instruments with infrared spectrometry and tuned lasers highly selective.

The principal characteristics of these laser systems are as follows:

- **High resolution:** Minimum interference with other gases, as well as linear response across a wide range of concentrations.
- **High radiation intensity:** This characteristic allows obtaining fast system responses (normally 1-2 seconds) and high sensitivity. This enables measuring concentrations at ppm levels and when an appropriate configuration is in place, parts per billion (ppb).
- **Robust instruments:** The equipment is small and able to withstand different ambient conditions (laboratory and industrial).
- **Single-component analysis:** The principal disadvantage of these instruments is that as a specific absorption band of the spectrum is selected, they can only determine the chosen compound.

The laser analysis equipment used in this study has been the "Boreal Laser Gas Finder FC" (hereafter LASER). This instrument has different configurations depending on the type of measurement to be made, and can be used for example in the open field for measuring fugitive emissions, or in stacks for measuring channelled emissions. In ceramic industry emissions, a configuration has been designed for in-stack measurement, since in this industrial process, the fugitive emissions of fluorine compounds can be considered negligible. The system was adjusted to detect the specific absorption band of the HF molecule.

Figure 1 schematically illustrates the operation of the instrument and the probe designed for in-stack sampling.

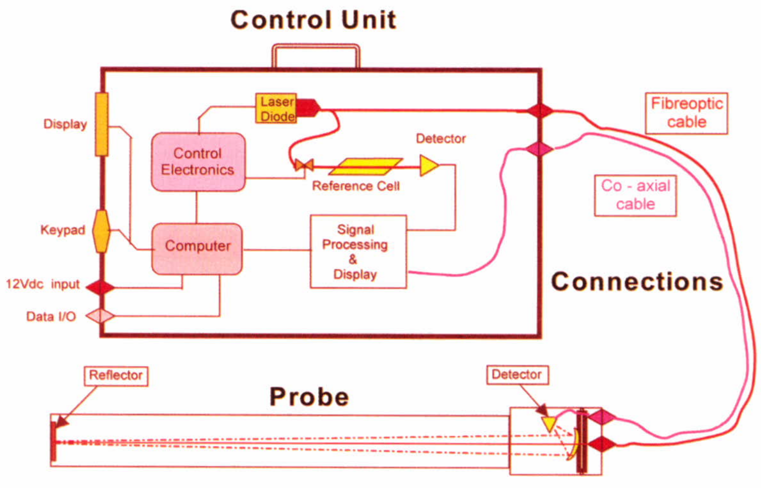

Figure 1. Schematic illustration of the equipment used.

One of the basic features of this instrument is that it has a continuous calibration system, in which a fraction of the generated laser radiation passes through a reference cell with a known HF content. This enables comparing measurement and reference signals to determine whether the absorption peaks coincide (Figure 2a) or not (Figure 2b). The comparison is quantified by means of a correlation coefficient (R^2), which indicates the similarity in the band emitted by the sample and by the reference. Reliable measurements require the values of R^2 to be close to one[14].

Furthermore, using the reference cell signal, the system has an algorithm that allows continuous zero adjustment.

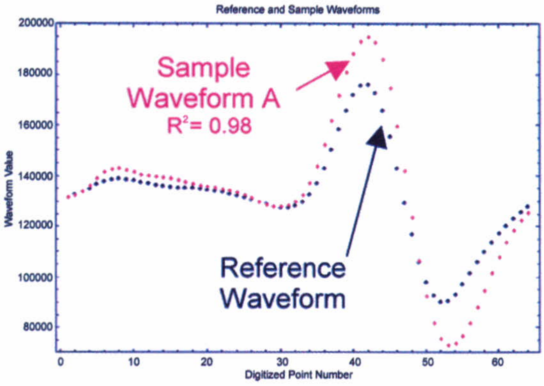

Figure 2a. Comparison of reference cell and sample A signals.

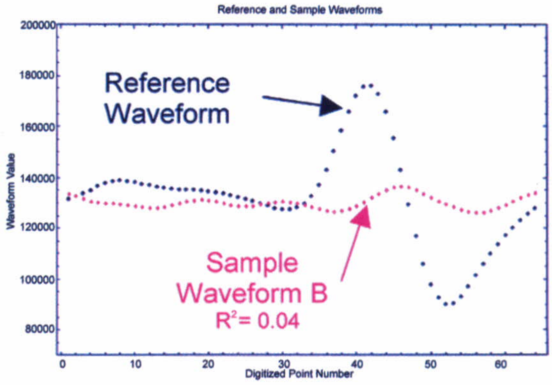

Figure 2b. Comparison of reference cell and sample B signals.

From a practical point of view, the fact that the analyser has a self-calibrating system is of enormous importance, as no standard gases need to be used, which simplifies the fieldwork.

2.4. STANDARD METHOD

In this study, the analysis data obtained with the LASER system have been compared with a standard method (chemical method).

Current standard methods used for determining fluorine compounds in the gaseous phase are based on extraction of a known volume of gases by an appropriate probe, and putting this through an absorption system that captures these compounds. An analytical determination of the fluorine present in the capturing solution then follows (specific method) and the fluorine concentration in the gaseous stream is calculated.

Various standard methods are found in the literature for the determination of fluorine compounds in gas emissions, in which a series of requirements is defined for appropriate test performance[4][15-18].

The determination of the fluorine compound concentration in ceramic industry emissions presents serious difficulties, stemming from the fact that these emissions contain low fluorine concentrations in a very reactive form. According to the literature surveyed[5], the fluorine present in these emissions is fundamentally found as HF.

In this study, the standard method used has been a test method fine-tuned at ITC, based on the application of American and Italian standards[2] [15-18]. At ITC it has been verified that at hydrofluoric acid concentrations of the order of 10-50 mg/Nm^3, which are the usual values in traditional ceramics kiln emissions, the concentration obtained by this method has a margin of uncertainty of about ± 10%. This uncertainty is of the order indicated in the consulted literature[18].

Previous ITC studies[3] have shown that this method provides good results in characterising these emissions, if the capturing system and sample analysis are strictly controlled. Note in this sense that it is fundamental to use materials in the probe that do not react with the fluorine present in the gaseous stream[5].

ITC is currently accredited by the Spanish National Accreditation Body (ENAC) for the determination of fluorine gas compounds by this method.

3. EXPERIMENTAL PROCEDURE

The experimental part of the present study consists of two different stages:

- Modification and adaptation of the instrument configuration for use in measuring the HF concentration in flue gases on firing ceramic tiles.
- Performance of sampling campaigns to verify the operation of the LASER system by comparison with standard methods and determination of the equipment's response capacity when modifications are implemented in ceramic tile firing processes. All the measurements have been conducted at industrial facilities.

3.1 MODIFICATION AND ADAPTATION OF THE LASER SYSTEM CONFIGURATION TO TRADITIONAL CERAMICS INDUSTRIES

On the basis of ITC experience in characterising gaseous emissions from ceramic kilns and knowledge of the facilities involved (accesses, stack diameters, number of samplings, etc.), a first prototype was designed that featured the following characteristics:

- **Sampling probe of fixed length.** A designed probe allowed performing measurements in practically all stacks with a single sampling opening. The probe itself acts as an emitter and receiver, and thus avoids problems of light beam misalignment caused by vibrations, incorrect emitter and receiver positioning, or problems of accessibility at two opposite points of the stack (180°).
- **Optic fibre and coaxial cable connections** integrated in the same tube to provide the wiring with greater robustness (great brittleness of fibreglass).
- **Lightweight compact control unit**. The standard control unit of the system suitably fulfilled portability and robustness requirements. No modifications were therefore implemented in this unit.

In making the first measurements we detected a series of problems that forced us to make certain changes in the initial configuration of the LASER instrument. These involved:

- Making the optic fibre and coaxial cable connectors, as well as the integrated cable that linked the probe to the control unit, more robust.
- Filtering the data obtained as a function of the R^2 factor values, as interferences were detected in some facilities because of the presence of magnetic fields.

- The high flue gas temperatures (150-220ºC) caused the probe electronics to heat up, in some samplings reaching temperatures above 50ºC. A cooling system was therefore designed for the probe electronics using compressed air from the facilities.
- Protecting the probe to enable performing stack measurements in adverse weather conditions.

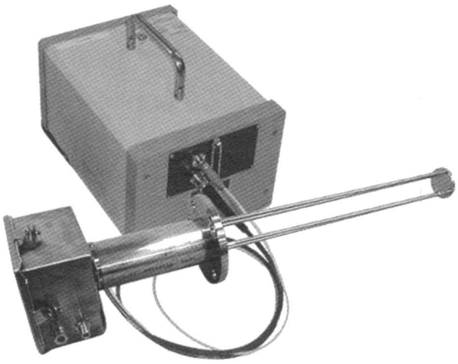

Figure 3. Photograph of the LASER equipment: probe control unit and final configuration.

3.2. MEASUREMENT CAMPAIGNS AT INDUSTRIAL FACILITIES

To verify the results a determination was conducted, as simultaneously as far as possible, with the LASER system and the standard method. The probes of both systems were positioned at points set as closely together as possible to assure equivalent gas samples and avoid dilutions or changes in temperature that could affect the concentration or nature of the fluorine compounds present in the gaseous stream.

The sampling train and test conditions in the standard chemical method are set out below:

- To avoid fluorine reactions with the metal and glass parts of the probe, these were lined with Teflon. It was verified beforehand that the type of Teflon used did not adsorb or release fluorine compounds in the test conditions.
- A non-heated probe was used in every case.
- The absorption system consisted of two bubblers that contained NaOH 0.1 N, a third empty bubbler, and a fourth bubbler with silica gel.
- Sampling was performed in non-isokinetic conditions, as the fluorine compounds were in the gaseous phase.
- The gas aspiration rate was held constant at values of the order of 5 l/min.
- The aspired gas volume always exceeded 200 litres (equivalent to about 45 minutes' sampling).
- Fluorine analysis in the capturing solution was by the potentiometric method with a fluorine ion selective electrode, in accordance with standard ASTM D1179.

With regard to the LASER equipment operating conditions used in the measurements, these were as follows:

- **Integration time:** The instrument's own configuration allows selecting different integration times (number of measurements saved per unit time). In the present study, readings were saved every 2 seconds, i.e., the minimum integration time that the instrument allowed.
- **Level of fluorine concentration:** In the case of emissions generated in the ceramic tile firing stage, the fluorine emission range is low (the equipment enables a priori selection of a high or low concentration measurement range).
- **Correlation coefficient (R^2):** Fluorine concentrations whose value of R^2 exceeded 0.95 were taken as valid values. The physical meaning of this parameter has been set out in point 2.3.
- **Other considerations:** A further important instrument operating parameter is emitted light intensity. In this case, as the equipment provides a continuous reading of this value, the system was run at light values above 800 mV.

4. RESULTS

4.1. VERIFICATION OF THE LASER INSTRUMENT RESULTS

To verify the results obtained with the LASER instrument, these have been compared with the results of the analyses set out with the standard chemical method. As all the determinations have been carried out on an industrial level, the first task was to select industrial facilities that had emission levels with significant differences in fluorine compound concentrations in the stack, with a view to validating instrument operation in the typical range of fluorine concentrations present in flue gas emissions from ceramic facilities.

The results obtained in these determinations are detailed in Table 1

Test	**Fluorine content (mg HF/Nm^3)**	
	LASER	**CHEMICAL METHOD**
1	20.7	25.4
2	8.7	10.1
3	5.6	6.4
4	17.9	18.8

Table 1. Results of fluorine gas determination in gaseous streams.

Figure 4 plots the fluorine concentration data obtained by the LASER instrument versus the values obtained with the standard method.

Despite the limited number of values, good correlation between both measurements can be observed, taking into account that each of these corresponds to a measuring time of about 50 minutes. Since the LASER instrument is only able to determine HF molecules, the results obtained indicate, as reported in the literature, that fluorine emissions in ceramic industry combustion kilns occur fundamentally in the form of hydrofluoric acid (HF).

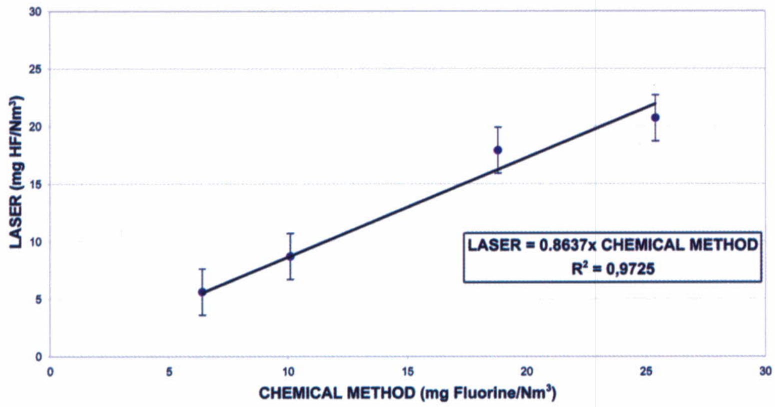

Figure 4. Correlation between the values of the LASER instrument and the standard chemical method.

4.2. ON-LINE MONITORING OF HF EMISSIONS

After validating the LASER results, we conducted a series of industrial tests to monitor HF emissions in different kilns under standard running conditions, as well as after performing different operations in these kilns, to observe the instrument's response capacity.

4.2.1. Tests conducted in kilns under standard operating conditions

A series of determinations was performed of the evolution of HF concentrations under standard running conditions in several red stoneware, porous wall tile and porcelain tile firing kilns.

From the point of view of the evolution of the HF concentration with time, the results obtained were very similar in every case, though obviously the absolute values of the concentrations varied depending on the size, type of product, etc. As an example, Figure 5 shows the evolution of these concentrations, under standard kiln operating conditions (without changes of size, cycle, etc.) with time. In this figure the variation in emission concentrations is observed to fluctuate in a relatively narrow margin, with only light swings around a mean value, which to all practical purposes can be considered constant.

The results indicate that to determine the HF concentration released by a kiln working under standard conditions, the batch sampling procedure is adequate, as the variation of the concentrations is not very significant across time, and can be characterised appropriately as a mean concentration.

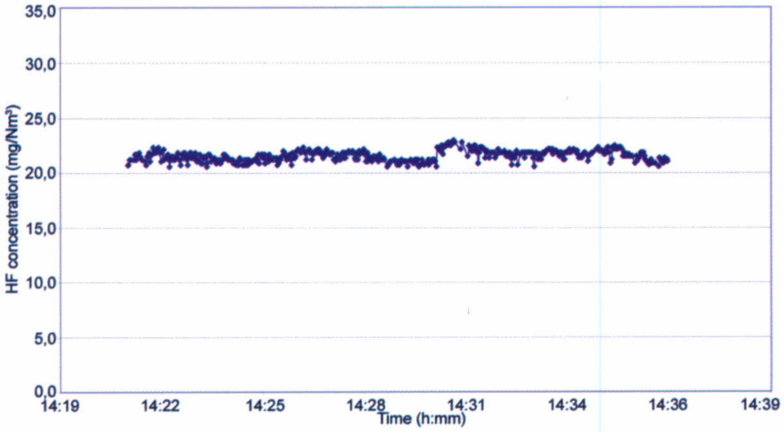

Figure 5. Example of the evolution of the HF concentration under standard operating conditions.

4.2.2. Tests conducted on implementing modifications in the kiln

The evolution of the fluorine concentration was monitored in the flue gas emissions when a size change was performed in a kiln that was fabricating red stoneware tiles under standard operating conditions.

This action was chosen for monitoring, because in this case, the product changeover involves stopping the kiln feed for a few minutes, and it was sought to monitor an action that produced a typical abrupt change in the manufacturing process.

Figure 6 displays the results obtained. It can be observed that introducing variations in the process generates important changes in the evolution of the HF emissions. In this case, the variation involved produced a sufficiently rapid response of the recording measurement system. The LASER instrument is therefore considered to display an appropriate sensitivity and rate of response to enable monitoring industrial kiln emissions.

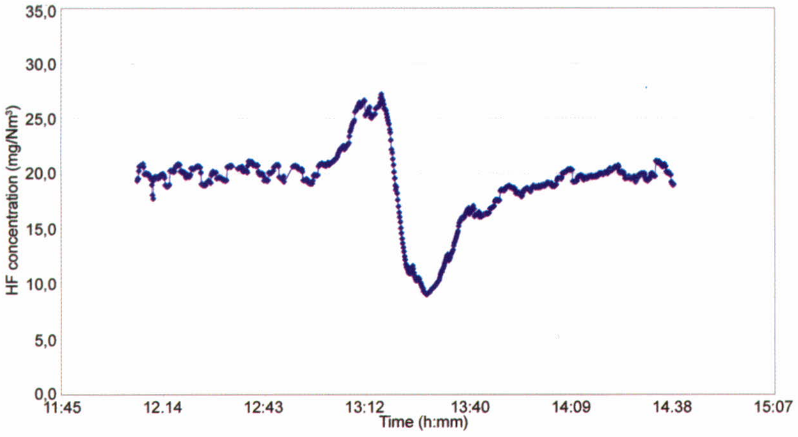

Figure 6. Evolution of the HF concentration on implementing modifications in the kiln.

4.2.3. Tests implementing changes in a HF treatment system

Finally, an industrial facility was chosen that had a gas cleaning system. The specific facility involved in the study has a treatment system in which $Ca(OH)_2$ is injected as a reagent. This reacts with HF to form CaF_2, a solid compound that is separated from the gaseous stream by means of a baghouse filter.

The on-line LASER measuring instrument was used in this facility to monitor the evolution of the HF concentration in the baghouse output, when different quantities of $Ca(OH)_2$ were proportioned.

Figure 7 shows a part of the results obtained during the study devoted to optimising the proportioned reagent quantity. It can be observed that when this quantity changes, the evolution of the HF emission varies with time; progressively increasing the quantity produces an ensuing reduction n the absolute value of the HF concentration in the emission.

As in the previous case, the rapid rate of response of the measuring equipment allows monitoring the evolution of the HF emission in real time. This confirms its potential as a tool of remarkable interest for studying the optimisation of the operating conditions of HF emission treatment systems in ceramic tile firing kilns.

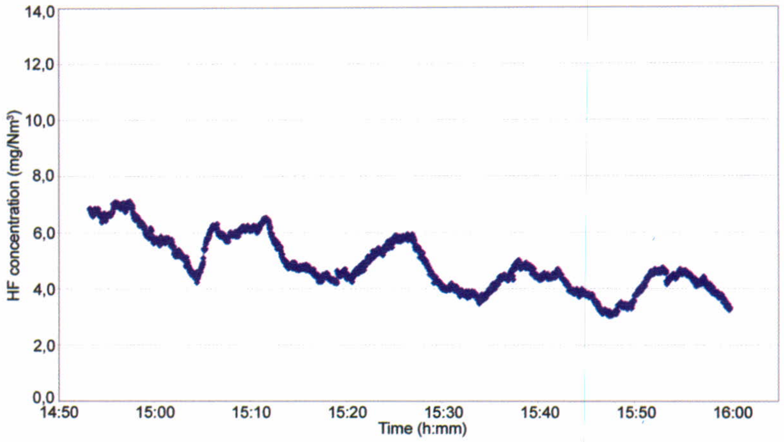

Figure 7. Evolution of the HF concentration on implementing modifications in the gas treatment system.

5. CONCLUSIONS

- In the study performed, the HF concentrations determined in the emissions of several ceramic tile kilns with an on-line measuring system based on a laser technology were observed to correlate satisfactorily with the results obtained by a standard method based on the absorption of fluorine compounds in a solution and subsequent analysis by a selective electrode.
- As the values determined by the laser equipment, which is configured to detect a characteristic absorption band of the HF molecule, coincided with those of the method that measures all fluorine compounds, the results obtained indicate that the emission of fluorine compounds in combustion kilns for firing ceramic tiles essentially occurs in the form of this compound. This fact is consistent with the literature[6], which indicates that the fluorine emission in clays, in a medium in which water vapour is present (usual in-stack values of industrial combustion kilns are of the order of 5 to 10 vol%), occurs in the form of hydrofluoric acid.
- In the study performed to monitor the HF emission on-line under standard operating conditions at various industrial ceramic tile kilns making different products, the emission of this compound was observed to remain very steady with time, with only slight fluctuations occurring around a practically constant mean value.
- The laser equipment displays a very rapid response in accurately detecting variations in HF concentrations in tile kiln emissions and therefore allows monitoring the evolution of the HF emission concentration when implementing different actions in a kiln. In view of above, it may therefore be concluded that the LASER instrument is a tool that enables rapid characterisation of HF emissions, and is able to monitor variations in the system (product changeovers, kiln adjustments, proportioned reagent quantity in a treatment system, etc.).

6. ACKNOWLEDGEMENTS

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