METHODOLOGIES FOR THE DETECTION AND QUANTIFICATION OF PYRITE IN CLAY RAW MATERIALS

M.P. Gómez-Tena (1), **C. Machí** (1), **J. Gilabert** (1), **E. Zumaquero** (1)

(1) Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE)

Universitat Jaume I. Castellón. Spain

1. INTRODUCTION

Owing to the high competitiveness of the ceramics market, ceramics technical and quality requirements are ever higher [1]. A defect to be avoided by ceramics manufacturers at present is the materialisation of efflorescence, which frequently occurs on façades and roofs. This stems from a build-up of salts that crystallise on the ceramic surfaces [2]. The defect resulting from efflorescence does not just have a negative aesthetic impact (appearance of whitish stains), but it can lead to serious problems inside the microstructure of the materials, impairing their quality and reducing product service life.

The presence of efflorescence can stem from numerous causes. To be noted are, in particular, soluble salts or impurities such as the mineral FeS_2 [3], also known as pyrite, which generally decomposes in different steps between 400 and 500ºC, according to the following equations:

Figure 1. Pyrite.

$$FeS_2 + O_2 \rightarrow FeS + SO_2 \quad (1)$$

$$FeS_2 \rightarrow FeS + S \quad (2)$$

$$S + O_2 \rightarrow SO_2 \quad (3)$$

$$2FeS_2 + (7/2)O_2 \rightarrow Fe_2O_3 + 2SO_2 \quad (4)$$

After the mineral has decomposed during firing of the product, part of the SO_2 is retained in the body, first forming intermediate compounds by reaction with species such as Na, K, Ca, and Mg that may be present in the ceramic raw materials [4], which favour the materialisation of efflorescence.

2. OBJECTIVE

The objective of study was the application of the combined technique of simultaneous thermal analysis coupled to a quadrupole mass spectrometer (TG-DSC-FTIR-QMS) for the determination and quantification of pyrite at trace level in ceramic raw materials that could generate efflorescence defects.

3. METHODOLOGY AND MATERIALS

The TG-DSC-FTIR-QMS technique was performed using a Netzsch TG-DSC model STA 449C Jupiter instrument coupled to a quadrupole mass spectrometer, model QMS 403 Aëolos®, and a BRUKER Fourier transform infrared (FTIR), model TGA-IR, spectrometer. The tests were conducted at a heating rate of 10ºC/min to a maximum temperature of 1200ºC.

The sulphur emission of the samples was determined by recording the signal relating to the mass-to-charge (m/z) ratio of SO_2, i.e. m/z 64, in the QMS, verifying the SO_2 emission and recording the spectra in the FTIR of the samples at different temperatures.

Calibration straight lines were constructed using a pure kaolin that contained no pyrites, to which known pyrite concentrations (0,05–0,5% pyrite) were added. The following products and raw materials were then analysed to quantify the sulphur emission:

- M1: Clay
- M2: Spray-dried powder for white-body tile
- M3: Unfired brick
- M4: Fired brick

Figure 2. TG-DSC sample holder.

4. RESULTS AND DISCUSSION

The recorded emissions for m/z=64, corresponding to the SO_2 emission for each of the standards of the calibration straight line, are shown in Figure 3. The characteristic pyrite emission can be observed, in a range from 250ºC to 600ºC, which followed a linear trend in the entire range of concentrations, allowing the emissions produced during thermal treatment to be quantified.

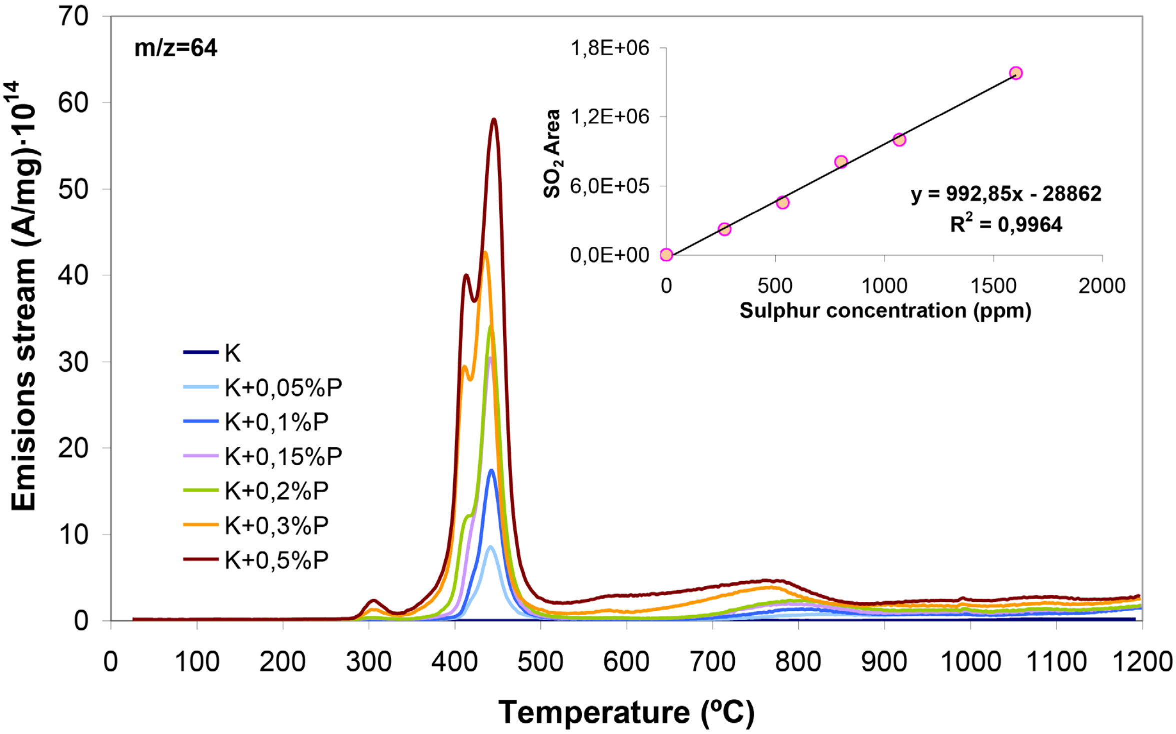

Figure 3. SO_2 emissions of the calibration standards.

The SO_2 emission was also recorded during thermal treatment of the different test materials, M1, M2, M3, and M4 (Figures 6, 7, and 8), in which the decomposition of sulphides (pyrites) and sulphates can be observed. The curves show the temperatures at which the sulphur compound emissions maximised.

Sample **M1**, corresponding to a clay, revealed the presence of pyrite, which decomposed between 400 and 500ºC, and a continuous emission starting at that temperature, which would correspond to decomposition of the different sulphates that formed as a result of the released sulphur that reacted with different elements in the clay. The quantity of sulphur released during the thermal cycle was 231 ppm sulphur.

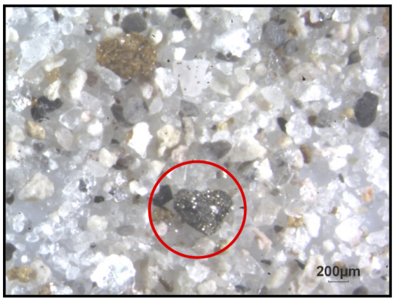

Figure 4. Magnifying glass photograph of pyrite traces in the clay sample.

Sample **M2** (spray-dried powder for white-body tile) exhibited sulphur emissions of pyrite as well as of different sulphates, as occurred in the clay, though the sulphur emission was much smaller, 65 ppm sulphur.

Figure 5. Efflorescence in a brick.

The study of materials **M3** and **M4** (unfired and fired brick) showed that the unfired material M3 released sulphur emissions at different temperatures. First, pyrite decomposed at temperatures between 400ºC and 500ºC, after which the sulphates decomposed in the unfired material, starting at 1000ºC.

The analysis results of the fired brick show that all sulphur emissions started at 950ºC, owing to sulphate decomposition. This was because the fired material no longer contained any type of sulphide in its composition and the sulphur released during industrial heat treatment had reacted with the ions present in the matrix (Na, Ca, Mg, K…) forming different types of sulphates. In the case of the bricks, this was because of the high calcite content in the unfired composition, mainly calcium sulphate.

The sulphur emissions produced by sulphate decomposition in samples M3 and M4 indicated that the sulphates present in the two samples had a different nature, as their decomposition temperatures varied slightly. The quantity of sulphur released in the samples was 71 ppm sulphur for sample M3 and 45 ppm sulphur for sample M4.

The sulphur emissions (ppm) produced on heat treating the different materials are detailed in Table 1.

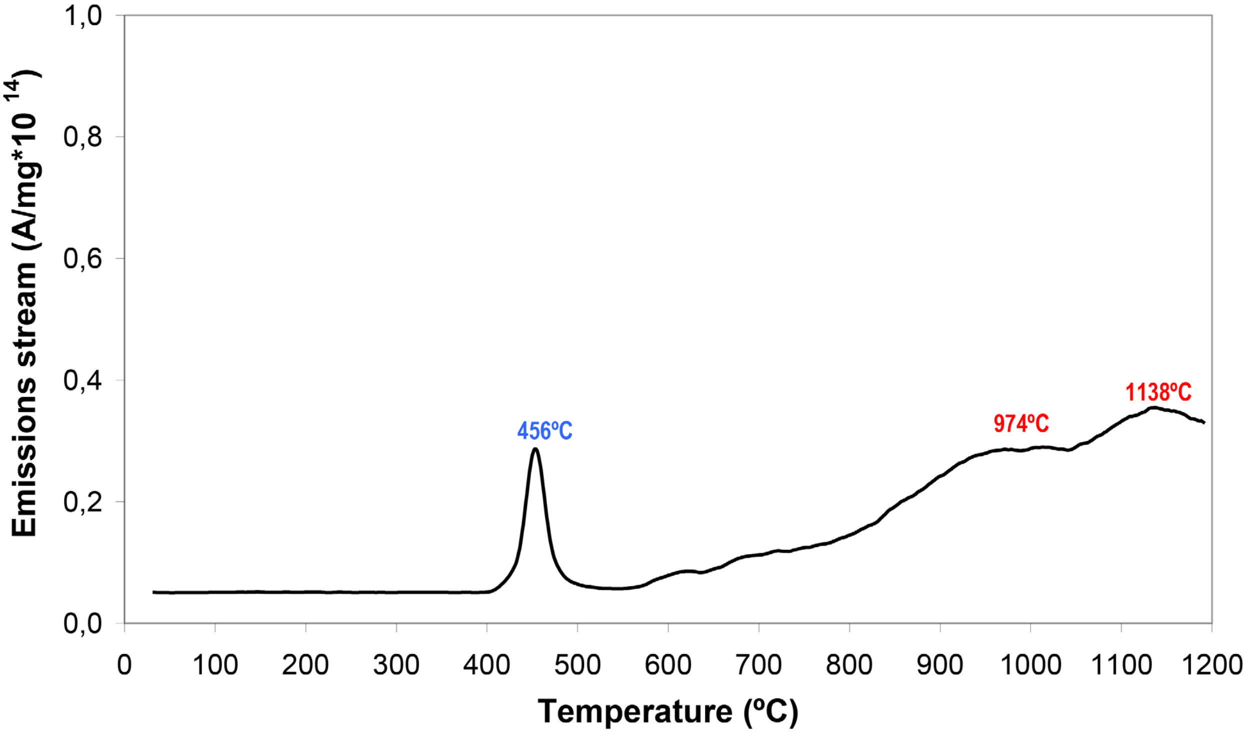

Figure 6. SO_2 emissions of sample M1 (clay).

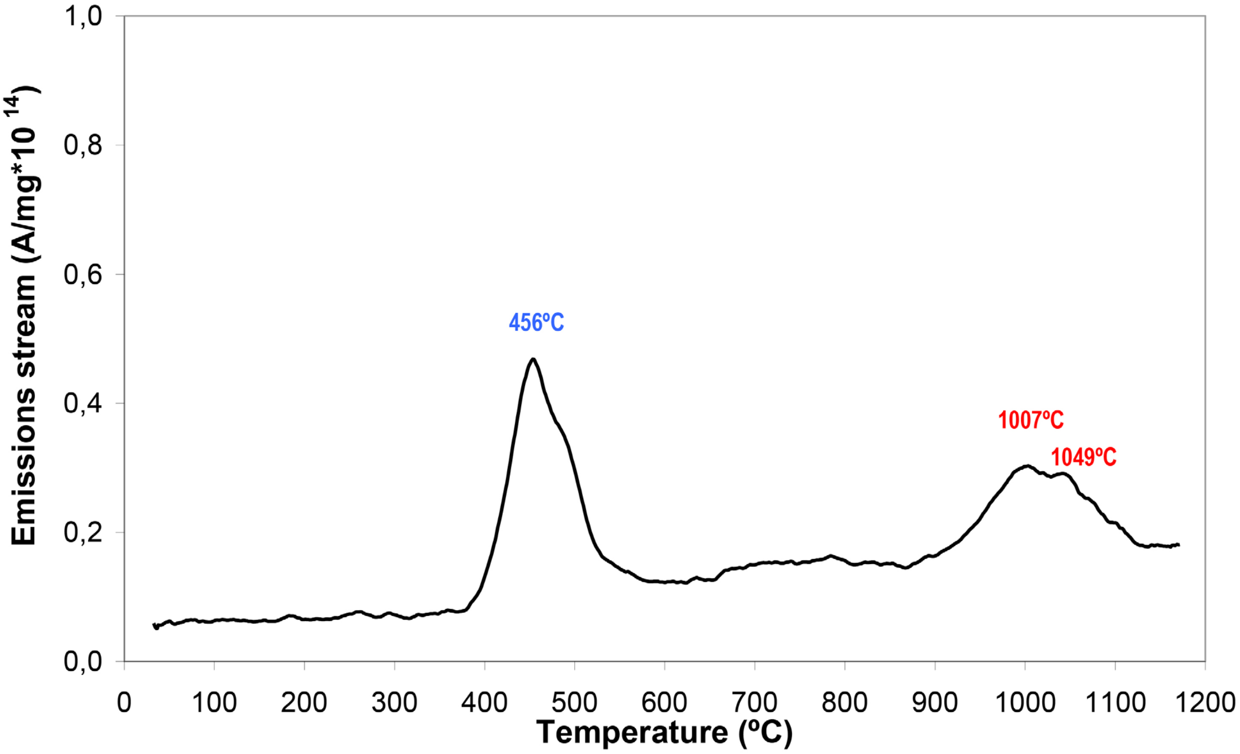

Figure 7. SO_2 emissions of sample M2 (spray-dried powder for white-body tile).

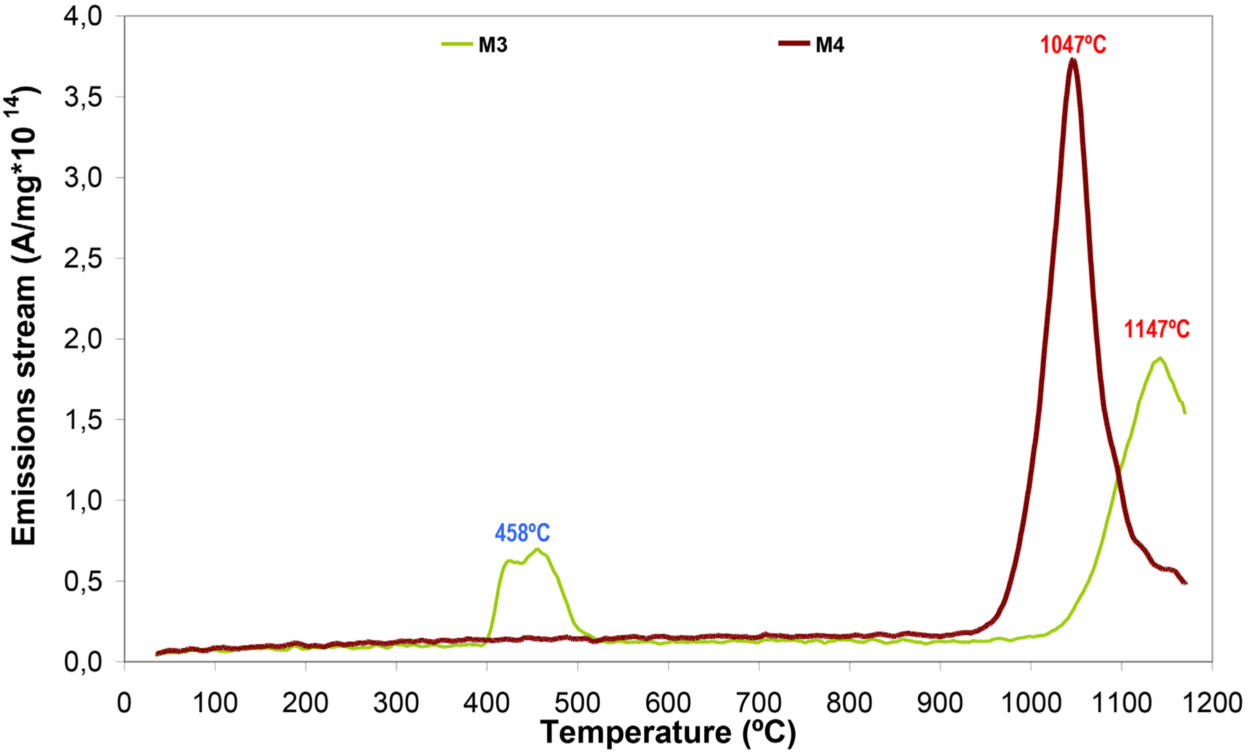

Figure 8. SO_2 emissions of samples M3 and M4 (unfired brick vs. fired brick).

	M1	M2	M3	M4
ppm S (pyrite)	41	34	32	-
ppm S (sulphates)	190	31	39	45
ppm S (total)	231	65	71	45

Table 1. Released sulphur concentrations (ppm) in the raw materials.

5. CONCLUSIONS

The results obtained in the analysis of the different studied materials show that the EGA (evolved gas analysis) technique allows sulphur compound emissions to be studied, even at trace level.

On the other hand, the technique also enables the sulphur emissions produced by sulphide (pyrite) impurities or sulphates of different nature to be differentiated. The appearance of efflorescence can thus be controlled either by decreasing the peak temperature of the industrial firing cycle or by incorporating additives such as ammonium lignosulphate or barium carbonate, which assist in reducing the salts responsible for efflorescence, into the starting composition.

6. ACKNOWLEDGEMENTS

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