VOC EMISSIONS IN THERMAL PROCESSES

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In recent years, the use of raw materials of an organic nature for ceramic tile manufacture has grown substantially, these materials being incorporated into the composition of both tile body and decoration materials. The use of organic compounds in body compositions stems from the need to assure certain key characteristics, such

as deformability and green mechanical strength, these being very important in the large sizes currently being produced. In the case of decoration materials, the new digital printing technologies require use of organic solvents for application through inkjet printheads (Dondi, Blosi, Gardini, & Zanelli, 2012)(VV.AA., 2018)

One of the environmental problems resulting from the use of these organic materials is the emission of VOCs, mainly in the ceramic tile firing stage (Gomar, Monfort, Escrig, Martinez, Rueda, 2012). The atmospheric impact of VOCs is related to their consideration as tropospheric ozone precursors and also to giving rise to odours that may sometimes be annoying, both inside ceramic tile manufacturing facilities and in the area surrounding them, therefore requiring appropriate solution from a scientific and technical viewpoint (Ferrari & Zannini, 2017).

In this study, procedures were developed and tested for the determination of VOCs without altering the physical characteristics of these emissions with continuous *in situ* samplings, which allow the emissions generated on an industrial level to be reproduced on a pilot scale. In particular, the implemented automatic measurement system enables determination of the total mass concentration of organic gaseous species by a flame ionisation detector (FID), according to standard UNE-EN 12619:2013, and quantification of individual gaseous species, including simple organic compounds by coupling of a Fourier transforms infrared (FTIR) spectroscopy system, according to technical specification CEN/TS 17337:2019.

The experimental work was carried out in two differentiated scenarios: an electric batch muffle kiln and a pilot-scale gas-fired continuous roller kiln. The two heating systems exhibited differences with regard to the composition of the atmosphere in contact with the tiles being processed, owing to the presence of water from natural gas combustion, and in regard to the related movement of the gases. Thus, in the case of the muffle kiln, the atmosphere was static and gas movement was solely due to the natural convection generated by the temperature gradient existing inside the muffle kiln. On the other hand, in the gas-fired pilot kiln, forced convection assisted by a fan extracting the gases generated inside the kiln caused the gases to circulate countercurrent to the tile feed in accordance with the kiln static pressure curve.

In both cases, ceramic tiles from industrial production lines, formed by pressing and decorated by inkjet technology, were used. The tiles were subjected to thermal cycles that reached peak temperatures of 700 ºC.

The results obtained in the electric muffle kiln show that VOCs were emitted upon application of the decoration onto the ceramic tile. This emission quickly increased with the thermal cycle until the emission peaked at a temperature of about 200 ºC, which indicates that they were compounds generated in the first kiln modules. The emission then gradually decreased, to practically disappear from 450 ºC on. On raising the amount of ink applied, the shape of the emission was maintained, but the emission peak value increased (Figure 1).

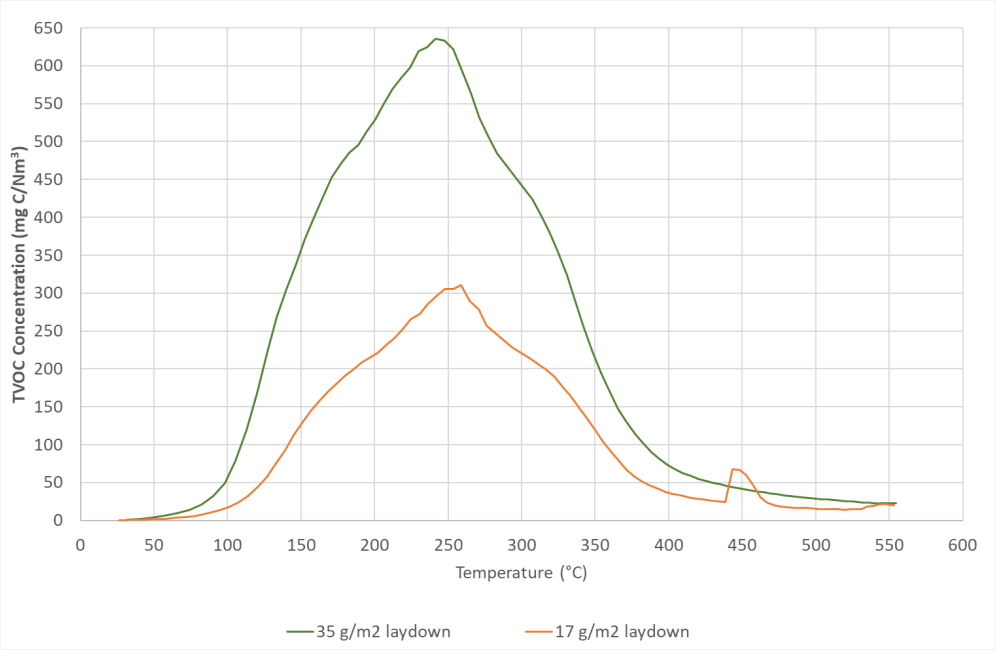

Figure 1. *TVOC emission in the electric muffle kiln as a function of ink g/m² laydown*

The measurement system implemented in this study was tested in the gas-fired pilot kiln, where the results obtained were of the same order of magnitude as those obtained in an industrial kiln. Although tile processing in the kiln was limited, the method developed exhibits great potential, as it allows organic compound emissions to be related to different manufacturing variables, such as different amount of organic compounds applied, compound formulation and chemical composition. In this sense, a very wide field of work opens up for developing inks with low VOC emissions.

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