TOC, Total Organic Carbon as an Indicator Parameter of Combustion. A New Methodology for the TOC Determination Directly on Fly-Ash from MSW Plants

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Introduction

It is now well-known that the solid, liquid and gaseous emissions from incineration plants contain many different classes of organic compounds, halogenated derivatives included.

Moreover, the organic compounds present in the solid matrix determine the behaviour and fate of micropollutants in combustion plants.

The organohalogenated classes in the emission from incineration plants are composed by different congener groups, *i.e.* same degree of chlorination, and each congener group is made up of isomers. The qualitative and quantitative determination of the congeners and isomers is time- and cost-demanding and it requires specialized laboratories and well-qualified staffs.

Good incineration plant management requires the complete combustion of organic materials as well as the immobilization of inorganic ones. To do this, on-line monitoring or, at least, analysis performed in short time is needed; these requirements are not compatible with time and cost involved by the specific analyses. For this reason it should be useful if indicators, or surrogate, parameters are available as a screening test to identify the presence of organic compounds in the emissions.

Objective

The purpose of our research project is to find, if exist, a correlation between the degree of mineralization of fly-ash and one or more combustion parameters in order to have a simple and quick indicator for plant management.

To evaluate the degree of mineralization of fly-ash, an obvious parameter is the TOC. For liquid samples, the TOC content is now largely used and several instruments and methodologies are available. For solid samples there are two main methodologies: an indirect one which requires the extraction of organic compounds from the solid matrix followed by the usual analytical procedures and a direct one involving the analysis of the solid samples.

Our goal is to set-up a quick methodology for the TOC measurement directly on the solid matrix when the concentrations are lower than 10 000 ppm, *i.e.* of the order of magnitude usually found in fly-ash from incineration plants.

Experimental

Total organic carbon (TOC) has been measured using a Dorhmann instrument built up with the standard module DC-90 and the S/SS accessory for solid matrix.

For liquid samples, the equivalent concentration of TOC is determined by calibration of the instrument with a known concentration of a standard organic compound dissolved in bidistilled water. The lowest detectable limit is 1 ppm of carbonium.

In principle, the procedure for solid samples is very simple. First the sample is put into the boat, the solid sample hatch is then closed and the boat is slid smoothly into the combustion zone for the analysis. Unlike the liquid analyzer, the solid module has not a pre-calibration range. Therefore, it was necessary to do a preliminary study to determine the relationship between the weighted sample introduced into the boat and the detected amount in function of the selected range of the NDIR detector (three range possible).

The setting-up of the methodology has presented some problems. First of all the choice of the "solvent". In fact a solvent must presents some general requirements: TOC equal to zero; granulometry large enough to avoid the drag along the furnace due to the flow of the carrier gas, and small enough to obtain a good mixing with the solute; thermal resistance large enough to avoid the formation of superficial crusts and the consequent absorbing of unburnt solute; properties and characteristics similar to those of the inorganic fraction of the sample being examined (fly ash from incinerators).

Following a series of preliminary tests, sodium sulfate was selected

The preliminary analysis on sodium sulfate show us that that the apparatus response to this solute is non equal to zero. Several analyses on different sample of sodium sulfate were performed and a value of a TOC about 335 ppm was found.

As "solute" was chosen the hydrogen potassium phthalate ($C_8H_5O_4K$, KHP), the same standard used for the calibration of the module for liquid samples analysis.

Solid mixtures of sodium sulfate with different weighting fraction of KHP were prepared in order to find the calibration curve. The solid mixtures are homogenized with a ball mill. The effects of ball dimensions as well as of speed and crushing time were tested.

The calibration curve was determined with analyses made in constant oxygen flow of 200 ml/min and a furnace temperature of 825 °C.

Finally, several analyses were performed on fly-ash from the electrostatic precipitator (ESP) and from the boiler of a real MSW incineration plant to evaluate the content of unburnt organic material.