

Direct Analysis of TOC on Fly Ash: Refinement of the Methodology

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1. Introduction

In a previous work¹ we presented a quick methodology for the direct determination on fly ash of the mineralization degree, or residual content of organic carbon, measured as Total Organic Carbon (TOC).

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

To obtain TOC values for fly ash within the instrument's optimal measurement range a "solvent" to "dilute" the fly ash must be chosen. The ideal solvent should be silicium dioxide, SiO₂, especially because his properties and characteristics are similar to those in the inorganic fraction of fly ash. Unfortunately the SiO₂ available at that time had very fine particles thus creating a lot of problems due to the trapping of silicium dioxide by the carrier gas and to concentration variations.

Sodium sulfate was selected as solid support after several attempts, although it was a less "realistic" solvent. In addition, the TOC value of Na₂SO₄ wasn't equal to zero, but almost 500 ppm. We couldn't find out the reason for the interference, so it wasn't possible to measure TOC values of less than 500 ppm.

On the other hand, carbonates and hydrogen carbonates, if present in the samples, could eventually contribute to the formation of the carbon dioxide measured by the instrument.

The aim of the present work is to find out possible solutions to these problems and to set up the final version of the methodology.

2. Experimental and results

General aspects of the analysis have been already reported¹.

Potassium Phtalate Acid (KHP), Na₂CO₃, NaHCO₃, K₂CO₃ and CaCO₃ are commercial products (Analyticals RPE, Farmitalia, Milano) with purity 99.5%, 99.8%, 99.8%, 99% and 99.5% respectively as well as silica gel (Merck, grade 60, 230-400 mesh ASTM).

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To test the instrument response to the pure "solvent" silica gel, blank analysis, triplicate runs on several samples are performed. The instrument response is converted in units of "equivalent" carbon, C_2 , where the index 2 stands for the pure "solvent". The slope of the least squares regression line (102 ± 5 ppm, Figure 1) represents the relative carbon content, in ppm, of pure silica.

The instrument calibration curve is determined with homogenized solid mixtures of KHP and silica gel. Triplicate runs are performed on different weighting fractions. Results are reported in Figure 2.

Synthetic mixtures Na_2CO_3 -silica gel are used for the determination of the Total Inorganic Carbon, TIC. The linearity of the instrument response in the TIC measure is verified, Figure 3. To test the precision and accuracy of the method, TIC values are measured on mixtures of silica gel with Na_2CO_3 , $NaHCO_3$ and K_2CO_3 , Table 1.

Table 1. Total Inorganic Carbon (TIC, ppm) of pure compounds-silica mixtures

Compound	Experimental values TIC (ppm)	Mean value \pm sd	Theoretical value
$NaHCO_3$	1914 1872 2038	1941 ± 85	1980
Na_2CO_3	2141 2016 1875	2010 ± 133	2000
K_2CO_3	1963 2024 2105	2030 ± 71	2100
$CaCO_3$	2116 2098 1951	2055 ± 90	2000

For the determination of the carbonate content in fly ash samples, two different types of analysis are performed. First, carbonates are measured with thermogravimetry (TGA 7, Perkin Elmer, temperature range 50-900°C): the carbonate content is determined to be below the instrument detection limit, *i.e.* less than 1% of weight.

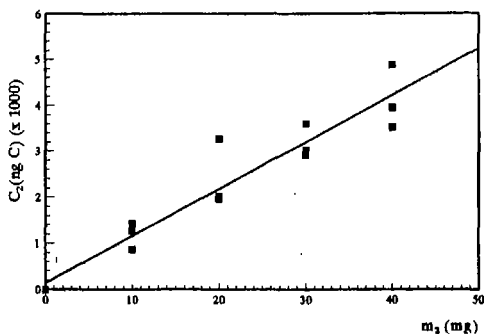
In the second series of analysis, 2 g fly ash react with 7 ml HCl 1 N. CO_2 is collected in 2 ml $Ba(OH)_2$ 0.4 N. The hydroxide excess is titrated with HCl 0.1 N (indicator: phenolphthalein). Six analysis on different fly ash samples are performed, the measure is always below the method detection limit.

The method detection limit was previously fixed to about 100 ppm, taking into account the instrument response for pure silica, and validated with blank runs on the Na_2CO_3 -silica mixture.

3. Discussion

Thanks to the silica selected, previous difficulties are overcome.

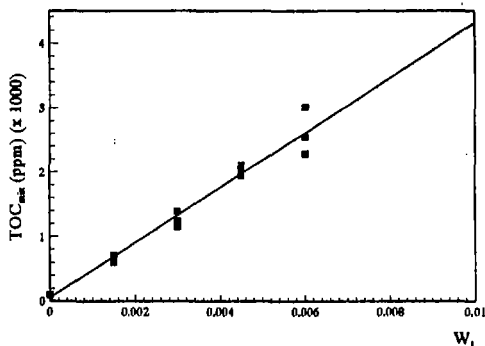
The instrument response for analysis on pure silica gel is 102 ± 5 ppm. We couldn't find out if the CO_2 measured has an organic (silica impurities) or an inorganic origin (CO_2



$$C_2 = (134 \pm 129) + (102 \pm 5) m_2$$

$$R^2 = 99.2\%$$

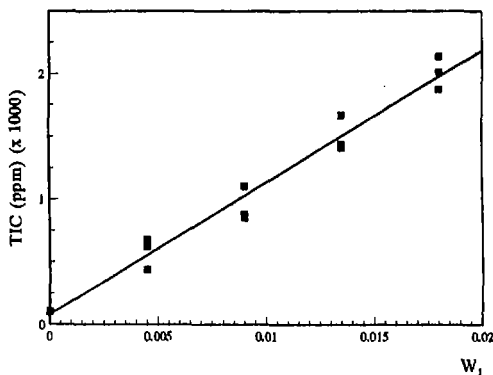
Figure 1 - Least squares regression line between absolute carbon content (C_2) and the weight of pure silica samples (m_2)



$$TOC_{mix} = (52 \pm 45) + (426233 \pm 12279) W_1$$

$$R^2 = 99.7\%$$

Figure 2 - Least squares regression line between TOC_{mix} and weighting fraction, W_1 , of the KHP solute for KHP-silica mixture



$$TIC = (78 \pm 42) + (105531 \pm 381) W_1$$

$$R^2 = 99.6\%$$

Figure 3 - Least squares regression line between Total Inorganic Carbon, TIC, and weighting fraction, W_1 , of the Na_2CO_3 solute in silica

adsorbed on silica).

Silica gel satisfies the requirements for a good "solvent", lowering the method sensitivity to 100 ppm, one fourth of the sensitivity achieved with sodium sulfate. This value is less than 5% of the medium TOC measured on fly ash. In any case, since silica contributes in a reproducible way to the TOC value, this contribution may be subtracted from the final data.

The linearity of the calibration curves measured with the SiO₂-KHP mixtures proves the method reliability, showing linear dependence of the TOC value on the weighting fraction. The experimental TOC of pure KHP, *i.e.* the slope of the least squares regression line in Figure 2, is in a quite good agreement with the theoretical and previously reported¹ values. As a consequence, it is possible to estimate the "true" value of the organic carbon.

Concerning the TIC determination, first of all the instrument response to synthetic mixtures of known inorganic carbon concentration is determined. Measured values are in good agreement with theoretical values, as reported in Tab. 1. The experimental TIC of pure Na₂CO₃, *i.e.* the slope of the least squares regression line in Figure 3, fits very well the theoretical value (TIC₁ = 113200 ppm).

For the determination of the carbonate and hydrogen carbonate contributions to the instrument response for fly ash samples, the TIC evaluated on the basis of two different analytical methods.

The first, thermogravimetric analysis, TGA, determines the carbonate content in fly ash to be below the instrument detection limit, *i.e.* less than 1% of weight.

The second analytical method takes into account the TGA detection limit and the instrument response for pure silica TOC. The method succeeds in determining the TIC value for Na₂CO₃-silica mixtures with an instrument response similar to the response of pure silica, *i.e.* 100 ppm. Analysis on fly ash samples determine a carbonate content of less than 50-60 ppm, which can be neglected if compared to the medium TOC value of fly ash.

4. Conclusions

The results show that the instrument response for fly ash is a real measure of the Total Organic Carbon, TOC, content of fly ash.

The method sensitivity is lowered to about 100 ppm using silica as solid "solvent".

TOC value has proven to be a reliable indicator of the mineralization degree of fly ash, directly determined on the solid matrix.

5. References

1 Lasagni M, Cosentino U, Moro G, Pitea D. Total Organic Carbon as an Indicator Parameter of Combustion: Setting-up of a Methodology for the Direct Analysis of Fly-Ash from Municipal Solid Waste Plants. In: Bonati L, Cosentino U, Lasagni M, Moro G, Pitea D, Schiraldi A, eds. *Trends in Ecological Physical Chemistry*. Amsterdam: Elsevier, 1993:253-74.