Evaluation of visible light reflectance measurement using an integrating sphere as a method of determining carbon content in fly ash

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Introduction

The content of unburned carbon in fly ash is one of the indicators that enable assessing the soundness of pulverized coal combustion in conventional utility power plants, and identification of the feasibility of using the generated ash as cement additives. With regard to the above, it is necessary to monitor carbon content in the aerosol stream of ash on-line, enabling thereby immediate adjustment of the operating conditions of the power boiler [1].

The most widely used industrial instruments for on-line monitoring include systems based on X-ray fluorescence and microwave resonance [2÷4]. Whereas the methods, the principle of which consists in the interaction of matter and radiation, include photoacoustic techniques, scattering of laser and visual light [5÷8]. Photoacoustic signal is generated by absorption of radiation by the sample placed in a tight chamber filled with gas (nitrogen, helium). Radiation absorbed by the sample raises its temperature, and consequently expands the surrounding gas. The heat wave passes through the surrounding gas and creates heat fluctuations of a frequency identical with the modulation frequency of the radiation, induces changes in gas pressure, and in consequence generates an acoustic wave, which is picked up by a highly sensitive microphone [9÷11]. One major limitation of industrial application of this method is the difficulty in placing the sample in the measurement chamber filled with inert gas, and also the high sensitivity of the measuring instruments to external vibrations. Optical methods, which utilize the phenomenon of light scattering, are based on the *Kubelka-Munk* law, which states that the intensity of scattered light depends on the concentration of the substance being determined in the sample [12, 13]. Samples of materials of rough surface and of powders are best tested using the method of scattered reflection, particularly the technique of an integrating sphere [14]. Specific features of this method make it suitable for testing fly ash samples differing in their shades of grey, which depend on the content of unburned carbon in the ash.

The purpose of the present studies is to verify the suitability of the measurement of visible light reflectance using an integrating sphere to determine unburned carbon content in fly ash.

Experimental

Test objects

The objects of studies were real samples of fly ash taken from the hopper of an electrostatic precipitator in a conventional power station fired with pulverized coal. The samples taken, the microscopic structure of which is shown in Figure 1, were subjected to laboratory tests to determine unburned carbon content. These determinations were carried out in the accredited analytical laboratory of the Operation Control Department of the Kozienice Power Plant. The tests were performed in accordance with an internal test procedure, designated PB-16/TECH and issued on 30 April 2009. Carbon content in the samples ranged from 2.30 to 5.08%wt/wt. The collected test material also included one sample of fly ash with carbon content of 13.13%wt/wt.

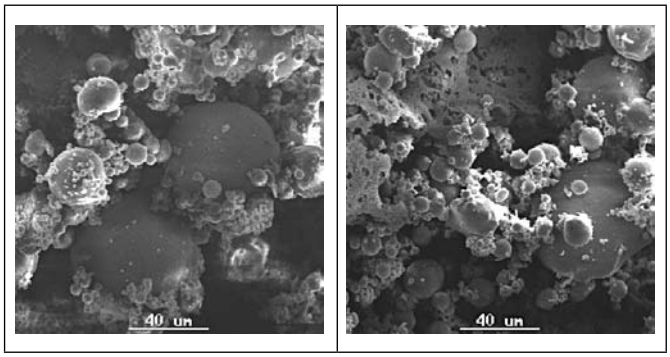

Fig. 1. Images of an ash sample taken with a scanning electron microscope (magnification 600x)

The ash samples contained mainly oxides of metals (iron, calcium, titanium), as well as aluminosilicates, or silica, which was unambiguously confirmed by analysis of EDS spectra, a typical example of which is shown in Figure. 2.

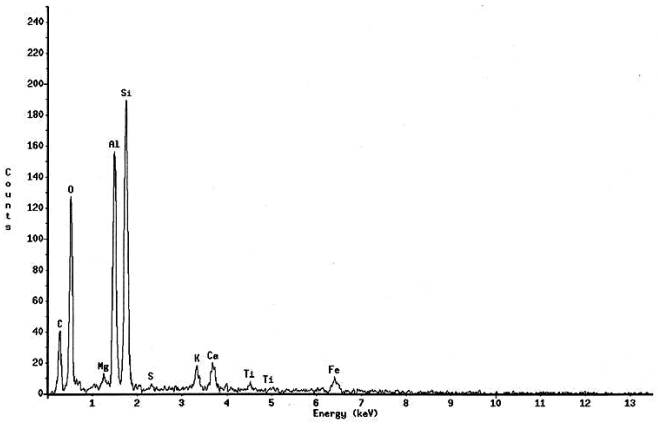

Fig. 2. EDS spectrum of an averaged fly ash sample

Samples of fly ash were subjected to spectral tests in order to correlate the results obtained with carbon content determinations carried out at the power plant, and to verify the selectivity, precision and sensitivity of the selected method of registering reflectance of visual radiation.

Methodology of spectral measurements

Determination of the amount of unburned carbon in ash was done by means of visual light spectrophotometry (400 to 800 nm), using a Jasco V-630 UV-Vis spectrophotometer. Measurements were made in the reflectance mode using an integrating sphere which collected light scattered by the ash sample placed in a special cell. The surface of the sample, which reflected and scattered the light, was in the shape of a disk 20 mm in diameter. A diagram of the optical system with the integrating sphere is shown in Figure 3.

The principle of sphere operation consists in focusing light from the monochromator onto a mirror, which directs the light beam through an

upper window in the sphere onto the sample. The sample was placed horizontally under the window of the measurement cell. The light beam hit the surface of the sample at an angle of 8° with respect to the normal to the surface of the tested material, and was then reflected and scattered. The diameter of the integrating sphere used in laboratory tests was 700 mm, and its internal surface was covered with a layer of barium sulphate.

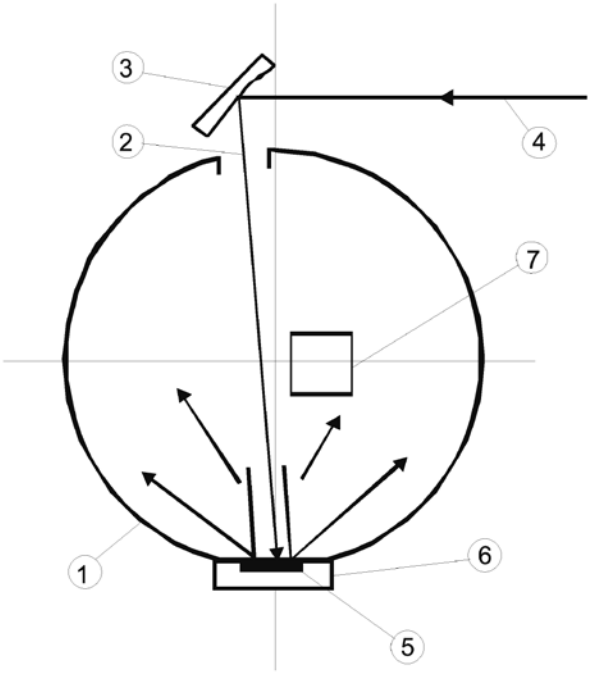

Fig. 3. Diagram of optical geometry of the integrating sphere used in spectral investigations to determine unburned carbon content in fly ash: 1) sphere 70 mm, 2) light beam inlet window, 3) focusing mirror, 4) monochromatic light ray, 5) test sample, 6) cell with sample, 7) solid state detector

Results and discussion

Reflectance curves of five selected samples of increasing carbon content were registered during preliminary laboratory work: 2.30%; 2.93%; 4.10%; 5.08%; 13.13%. The samples selected enabled to evaluate the suitability of the spectrophotometric method for on-line determination of unburned carbon in ash under industrial conditions within a broad range of analyte concentration in the matrix.

The results, in the form of spectral curves illustrating the dependence between reflectance and wavelength of visual radiation, are shown in Figure. 4.

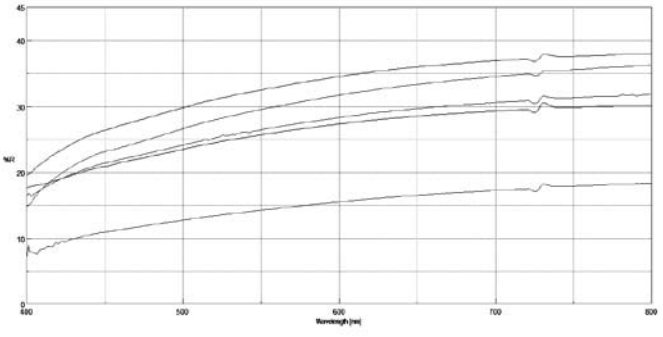

Fig. 4. Comparison of reflectance vs. visual radiation wavelength curves plotted for selected ash samples of the following carbon content: 1) 2.3% wt/wt, 2) 2.93% wt/wt, 3) 4.1% wt/wt, 4) 5.08% wt/wt, 5) 13.13% wt/wt

The presented curves indicate that the method applied enables identification of samples which differ in the content of unburned carbon, i.e. samples of lower carbon content show higher reflectance, whereas samples of high carbon content show low reflectance. Nonetheless the selectivity of the method depends on the spectral range of radiation used to illuminate the sample. Analysis of the relations between reflectance and visual radiation wavelength demonstrates clearly that the largest span of scattering by the sample is observed in the wavelength range of 400 to 440 nm. In this area, however, it is not possible to differentiate between samples of various carbon content. The curves presented in Figure 4 show that scattering of red light (wavelength 630 nm to 740 nm) is characteristic of each sample.

The change of reflectance in the red light range is only to a minor degree dependent on wavelength, which permits averaging of the analytical signal. Thus, for the purposes of fast industrial analysis, it is advisable to make measurements in the red light wavelength range. The tests carried out also established a correlation between carbon content and analytical signal obtained during spectral investigations. Figure 5 shows the relationship between light reflectance (wavelength 720 nm) and carbon content in tested samples of ash.

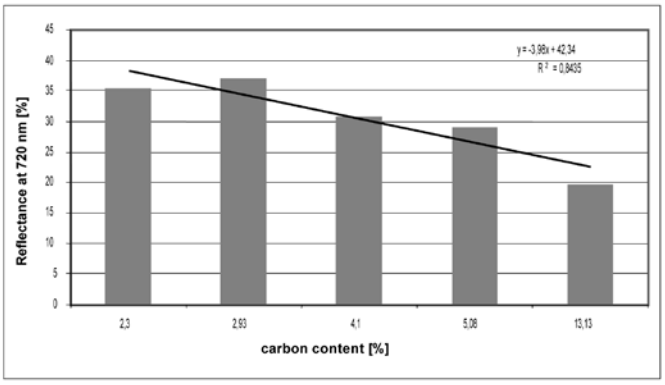

Fig. 5. Correlation between colorimetric analysis results and laboratory determination of carbon content in ash within a broad range of analyte concentration in the matrix

The results obtained confirm the linear relationship between reflectance of red light and carbon content in tested samples. The derived function equations have relatively high correlation coefficients ($R^2 > 0.8$). Linear dependence of the measurement signal on the measured quantity is the basic condition of applying a test method under industrial conditions. The sensitivity of the method has also been evaluated by measuring reflectance of ash samples between which the interval in experimentally determined carbon content was not more than 0.1%wt/wt. The results obtained are shown in Figure 6.

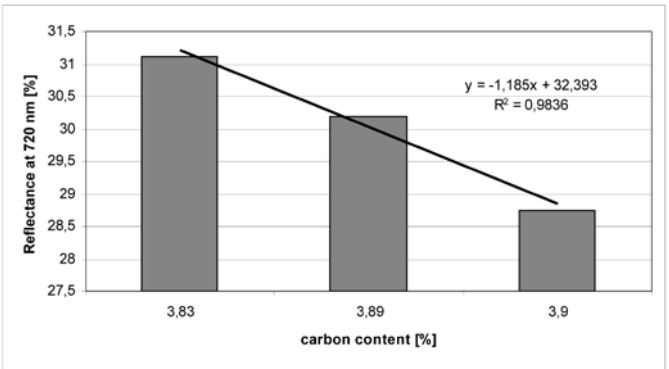

Fig. 6. Correlation between colorimetric analysis results and laboratory determination of carbon content in ash within a narrow range of analyte concentration in the matrix

Analysis of red light reflectance enables differentiation even between samples of similar concentration of unburned carbon (differences in the range of 0.1%wt/wt carbon), which is shown in Figure. 6.

The precision of the spectrophotometric method was also verified in laboratory tests. Samples selected for testing had unburned carbon content on both extremes of the range, i.e. one with carbon content of 2.3%wt/wt and the other 13.13%wt/wt. A series of ten measurements were carried out on each sample and standard deviation from the arithmetic mean was calculated. The results obtained are given in Table 1.

Table 1

Statistical evaluation of the precision of the method consisting in measuring sample reflectance at wavelength of 720 nm

Carbon content %(wt/wt)	Reflectance measurement results [%]	Arithmetic mean	Standard deviation
2.30	33.2; 33.7; 34.2; 34.3; 34.3; 34.4; 34.4; 34.8; 34.9; 35.5	34.4	0.6
13.13	17.4; 18.0; 18.3; 19.5; 19.6; 19.7; 20.0; 20.5; 20.7; 21.4	19.5	1.3

Statistical analysis of the results obtained indicates that the scatter of results around the expected value, expressed as standard deviation, is higher in the case of samples of higher carbon content (13.13%wt/wt) than those of low carbon content around 2.3 %wt/wt. The errors that occurred were probably due to non-homogeneity of the analytical material, difference in ash consolidation in the measurement cell, and also imperfect smoothing of the ash samples from which visual light was reflected. Nevertheless the values of standard deviation for the results of each measurement series indicates that the precision of measurements taken with a UV-Vis spectrophotometer equipped with an integrating sphere and operating in the narrow band of red light is high.

Summary

The investigations performed have initially confirmed the suitability of visible light reflectance measurement using an integrating sphere for the determination of unburned carbon content in fly ash generated during combustion of pulverized coal in conventional power plants. Comparison between the measured reflectance values for ash samples and unburned carbon content therein shows a linear correlation between these values. In addition it was established that the method featured high precision and sensitivity of spectrophotometric measurements, particularly within the wavelength range of red light, enabling identification of differences in analyte content in the matrix at a level of 0.1%wt/wt.

The relative simplicity of the method, linear relationship between the signal obtained and the content of unburned carbon in the ash sample, along with high sensitivity and precision, open ways for the method to be utilized in industrial on-line analysers.

Literature

1. Styszko-Grochowiak K., Gołaś J., Jankowski H., Koziński S.: *Characterization of the coal fly ash for the purpose of improvement of industrial on-line measurement of unburned carbon content.* Fuel 2004, **83,** 1847-1853.
2. Niewczas B., Pronobis M.: *Kontrola procesu spalania węgla w pyłowych kotłach energetycznych.* Zeszyty Naukowe Politechniki Opolskiej. Elektryka 2006, **315,** 56, 509-518.
3. Parus J., et al.: *Determination of the carbon in coal and ash by X-ray fluorescency.* X-Ray Spectrom. 2000, **29,** 2, 192-195.
4. Liu H., Tan H., Gao Q., Wang X., Xu T.: *Microwave attenuation characteristics of unburned carbon in fly ash.* Fuel 2010, **89,** 3352-3357.
5. Melick T., Sommer T., Conrads H.: *Real-time monitoring of unburned carbon on utility fly ash.* Proc. of NETL Conf. „Unburned carbon on utility fly ash" Lexinghton, 2005.
6. Iannone R.Q., Morlacchi R., Calabria R., Massoli P.: *Investigation of unburned carbon particles in fly ash by means of laser light scattering.* Appl. Phys. B 2011, **102,** 357-365.
7. Ouazzane A.K., Castagner J.L., Jones A.R., Ellahi S.: *Design of an optical instrument to measure the carbon content of fly ash.* Fuel 2002, **81,** 1907-1911.
8. Fan M., Brown R.: *Precision and accuracy of photoacoustic measurements of unburned carbon in fly ash.* Fuel 2001, **80,** 1545-1554.
9. Handke M.: *Metoda fourierowska i techniki pomiarowe stosowane w spektroskopii oscylacyjnej.* W: Handke M. (red.), Paluszkiewicz C. (red.): *Metody i techniki pomiarowe w spektroskopii oscylacyjnej.* Wyd. Akapit, Kraków, 1998.
10. Brown R.*: Method and apparatus of measuring unburned carbon in fly ash.* US Pat. 1991**, 5,** 069,551.
11. Fan M., et al.: *Relationship among loss-on-ignition and unbarned carbon and the FTIR photoacustic spectra of fly ashes.* International Journal of Environment and Pollution 2003, **19,** 3, 301-309.
12. Gołaś J., Jankowski H., Niewczas B., Piecha J., Szkutnik Z., Worek C.: *Ciągły pomiar węgla w popiele lotnym.* Prace Naukowe Instytutu Techniki Cieplnej i Mechaniki Płynów Politechniki Wrocławskiej 2000, **56,** 10, 279-288.
13. Gołaś J., Jankowski H., Niewczas B., Piecha J., Skiba A., Szkutnik Z., Worek C.: *Fotometryczny pomiar zawartości węgla w popiołach emitowanych podczas procesu produkcyjnego w elektrowni.* Elektronizacja – podzespoły i zastosowania elektroniki 2000, **9,** 18-22.
14. Lindseth I., Barda A., Spooren R.: *Reflectance measurements of aluminium surfaces using integrating spheres.* Optics and Lasers in Engineering 2000, **32,** 419-435.

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