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THERMAL ANALYSIS OF SOME FLY ASHES
I. Gastitrimetric determination of carbon and sulfur contents of fly ashes

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Abstract

The thermal behavior of different fly ashes from the electrical precipitators of various pulverized carbon fuel-fired boilers was investigated by means of simultaneous TG, DTG, DTA and EGA analysis. The carbon and sulfur contents of the samples were determined by gastitrimetry. The compositions of the samples were examined by X-ray diffraction. The quantitative oxide analysis of the ashes was carried out by means of a classical method.

Keywords: fly ashes, gastitrimetry, simultaneous TG–DTG–DTA–EGA, X-ray

Introduction

The chemical compositions and other properties of fly ashes are strictly dependent on the coal type used as fuel material and on the burning conditions in the boilers of the power station. Some coke residues and other combustible materials can remain in fly ash because of the low burning temperature resulting form the low caloric value of the coal. Combustible materials and some other components in fly ashes can be determined by means of thermogravimetric mea-surements. Additionally, the carbon and sulfur contents of the samples can be determined separately by means of gastitrimetry. The results of the thermal analysis can serve as a control of the processes in the boiler, and the boiler, efficiency can be improved by changing the burning conditions.

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Experimental

Materials

Fly ashes for thermal analysis were collected from the electrical precipitators of boilers fired with powdered carbons. The compositions of the fly ashes varied, depending on the coal type used as fuel. Fly ash samples 1 and 2 originated from bituminous coals, and samples 3 and 4 from lignites. The results of quantitative oxide analyses of the ashes are given in Table 1.

Table 1 Chemical composition of the ashes (weight %)

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
1	17–20	11–15	6–8	30–40	2–3	0.3–0.4	0.3–0.4	19–26
2	35–45	19–25	6–7	10–17	2–3	0.6–1.1	1–2	8–17
3*	51–79	9–20	2–6	5–11	1–3	0.2–1	1–2	3–7
4*	45–50	17–19	9–11	8–9	2–3	0.4–0.6	1–2	6–8

* Samples 3 and 4 contain TiO_2 (~1%) and P_2O_5 (~0.1%)

Techniques

Qualitative X-ray analyses of the ashes were carried out on an HZG-4/C diffractometer (Carl Zeiss, Jena), using CoK_α (λ=0.176 nm) radiation and a Fe filter. The speed of the goniometer was 1° min^{-1}. Diffractograms are presented in Figs 1a–d.

Simultaneous TG, DTG, DTA and EGA analysis [1] was carried out with homogenized original samples on a thermobalance type Derivatograph-C (Hungarian Optical Works, MOM, Budapest). The samples (~400 mg) were heated up to 1000°C at a heating rate of 10 deg·min^{-1} in an open platinum crucible in both oxygen and nitrogen atmospheres. Figures 2–5 show thermogravimetric (TG), derivative thermogravimetric (DTG), differential thermoanalytical (DTA) and thermogastitrimetric (TGT) curves of samples in an oxygen (Figs 2a–5a) or a nitrogen atmosphere (Figs 2b–3b). Thermogastitrimetry [2–4] belongs among the methods of EGA.

The gastitrimetric determination of the carbon and sulfur contents of the samples was carried out with a gas-titrator (Hungarian Optical Works, MOM, Budapest). For the determination of SO_3 and CO_2, the sample was heated in oxygen and nitrogen atmospheres at a heating rate of 10 deg·min^{-1}. The oxygen or nitrogen flow velocity was 35 $dm^3 \cdot h^{-1}$. For the determination of SO_2, the gases were flushed out and absorbed in an aqueous solution containing 3% ethanol and 0.3% H_2O_2 (H_2O_2 oxidizes SO_2 to SO_3). The gases were pumped through the absorber at a velocity of 10 $dm^3 \cdot h^{-1}$. The titration of SO_3 was carried out at $pH=4.3$ with 0.1 mol·dm^{-3} NaOH. The total amount of SO_3 and CO_2 was determined by automatic titration with 0.1 mol·dm^{-3} NaOH at $pH=9.3$. The quantity of CO_2 can be calculated from the difference between the volumes of NaOH used for the titration at $pH=9.3$ and at $pH=4.3$. For the pH measurements, glass indicator and calomel reference electrodes were used.

Results and discussion

X-ray analysis of the original samples showed that all of them contain α-SiO_2, $CaSO_4$ and α-Fe_2O_3 (Figs 1a–d). In addition to these components, sample 1 contains CaO and $CaCO_3$, sample 2 CaO, sample 3 FeS and sample 4 Al_2SiO_5. The components were determined by comparing the characteristic *d* values (calculated on the basis of the diffraction peaks from the Bragg equation) of the samples with the ASTM card data [5]. Some of the *d* values were not identified because of the lack of ASTM data.

The results of thermogravimetric analysis are given in Figs 2–5. Figures 2a–5a depict the derivatograms of the samples in an oxygen atmosphere. Samples 3 and 4 can be seen to contain a certain amount of adsorbed water (~0.3%). The adsorbed water evaporates up to 100°C. Above 100°C, structural water departs; this is probably the crystal water of $CaSO_4{\cdot}2H_2O$ because all of the samples contain $CaSO_4$ (Figs 1a–d). The water loss processes partially overlap, but the double peak in Fig. 3a supports this proposition: the literature data [6] indicate that $CaSO_4{\cdot}2H_2O$ loses its crystal water in a two-step process. The amount of water that departed in the temperature range up to 250°C varied from 0.1 to 0.5%.

In the temperature range from 300 to 500°C, all of the samples underwent a mass loss (TG and DTG curves in Figs 2a–5a) with an exothermic maximum (see DTA curves). In this temperature range, the burning of carbon or oxidation of some other components took place.

For sample 1 (Fig. 2a) the decrease in mass began at about 360°C, followed by an increase in mass at about 450°C (see TG and DTG curves), while only one exotherm appeared, with maximum at about 480°C (see DTA curve). The results of the X-ray analysis revealed that all the samples contained CaO, so the mass loss probably corresponded to the loss of water from $Ca(OH)_2$ or to the departure of CO_2 formed by burning. The increase in mass may be based on the reaction of this CO_2 with the newly formed CaO, or by oxidation of some other components of the sample, e.g. by oxidation of iron oxides.

The thermoanalytical curves of sample 2 (Fig. 3a) showed a mass loss process (see TG and DTA curves), with an exothermic maximum at about 400°C and an endothermic maximum at about 450°C. This means that at least two processes took place: probably the burning of carbon and the decomposition of

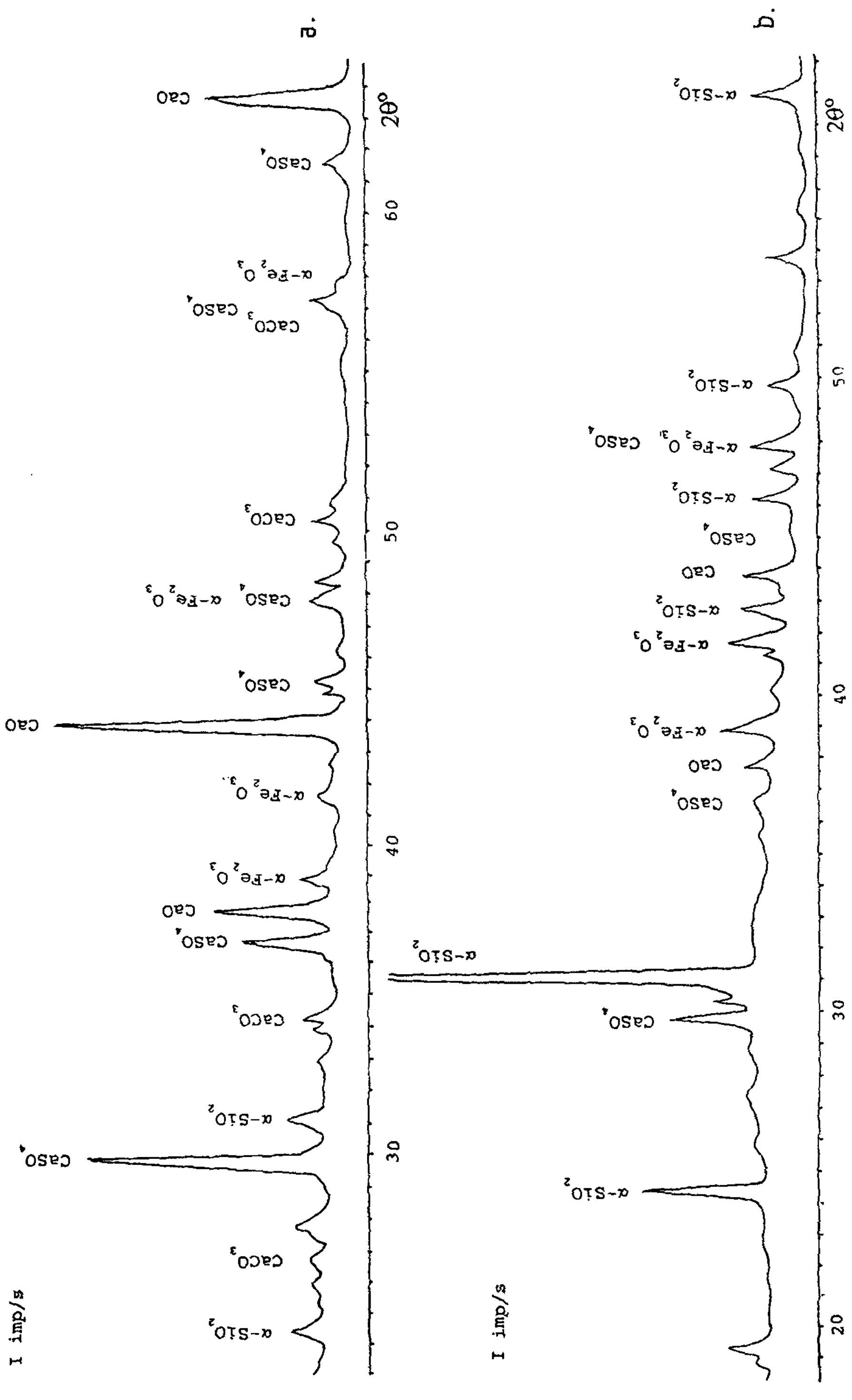

Fig. 1 Diffractograms of the fly ash samples: a) sample 1; b) sample 2

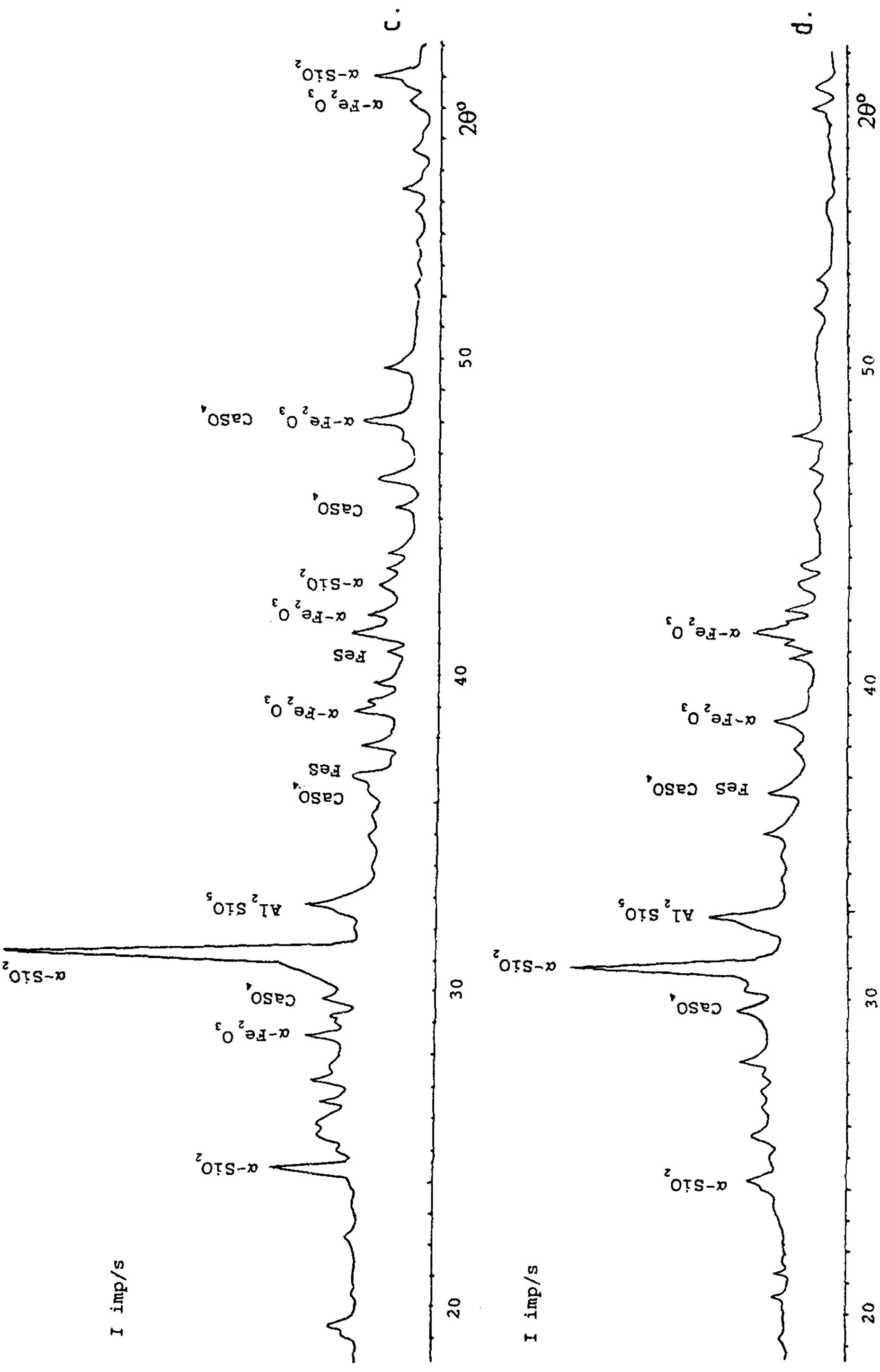

Fig. 1 Diffractograms of the fly ash samples: c) sample 3; d) sample 4

$Ca(OH)_2$. The temperature of the endothermic process corresponded to that for the loss of water from $Ca(OH)_2$ [7]. The mass loss corresponding to the dehydration of $Ca(OH)_2$ was about 0.3% in an oxygen atmosphere (Fig. 3a), while in a nitrogen atmosphere it was about 0.5% (Fig. 3b). This phenomenon suggests the possibility of a third reaction, i.e. the reaction of CO_2 formed by burning with the newly-formed CaO, to give $CaCO_3$.

The thermoanalytical curves of samples 1 and 2 revealed an endothermic mass loss process in the temperature range from 650 to 900°C (Figs 2a and 3a). The decomposition of $CaCO_3$ takes place in this temperature range [8]. In samples 3 and 4 (Figs 4a and 5a), there was no thermal change in this temperature range.

The formation of $Ca(OH)_2$ and $CaCO_3$ in the fly ash can be explained by the action of air on the samples: the moisture of the air reacts with CaO to give $Ca(OH)_2$, which, in contact with CO_2, forms $CaCO_3$.

To obtain more information on the above-mentioned processes, similar measurements were carried out in a nitrogen atmosphere. The peaks of the endothermic processes in the temperature range from 350 to 650°C may be completely covered by the large exothermic peak of the oxidation processes in an oxygen atmosphere. This happens in the case of sample 1 (Fig. 2a). A nitrogen atmo- sphere prevents all oxidation processes in this temperature range, so the mass loss process in this range can be related to the loss of water from $Ca(OH)_2$. The amount of hydrated CaO in the fly ash can be calculated from the mass loss of water. The hydrated CaO contents of samples 1 and 2, determined on the basis of the thermogravimetric data measured in a nitrogen atmosphere, were 2.5% and 1.2%, respectively. Samples 3 and 4 did not contain hydrated CaO (Figs 4b and 5b).

The thermoanalytical curves of samples 1 and 2 in a nitrogen atmosphere demonstrated that at about 750°C, before the decomposition of $CaCO_3$ was finished, some other reactions began. These are probably reactions of different iron oxides with solid carbon and other carboniferous products of the sample. In this temperature range, there is also a possibility of the decomposition of carboniferous compounds in fly ash. These processes are manifested in a significant mass loss and partially overlap the decomposition of $CaCO_3$.

In principle, the $CaCO_3$ contents of samples 1 and 2 could be determined on the basis of the TG curves, from the mass loss that begins at about 650°C or from the volume of NaOH consumed for the titration of CO_2 (TGT_{CO_2}). However, in an oxygen atmosphere, the CO_2 formed by burning of the carboniferous components of the sample partially reacts with CaO, formed by the decomposition of $Ca(OH)_2$, giving $CaCO_3$, and this decomposes simultaneously with the $CaCO_3$ content of the original sample. On the other hand, in a nitrogen atmosphere, the decomposition of $CaCO_3$ is interfered with by other decomposition

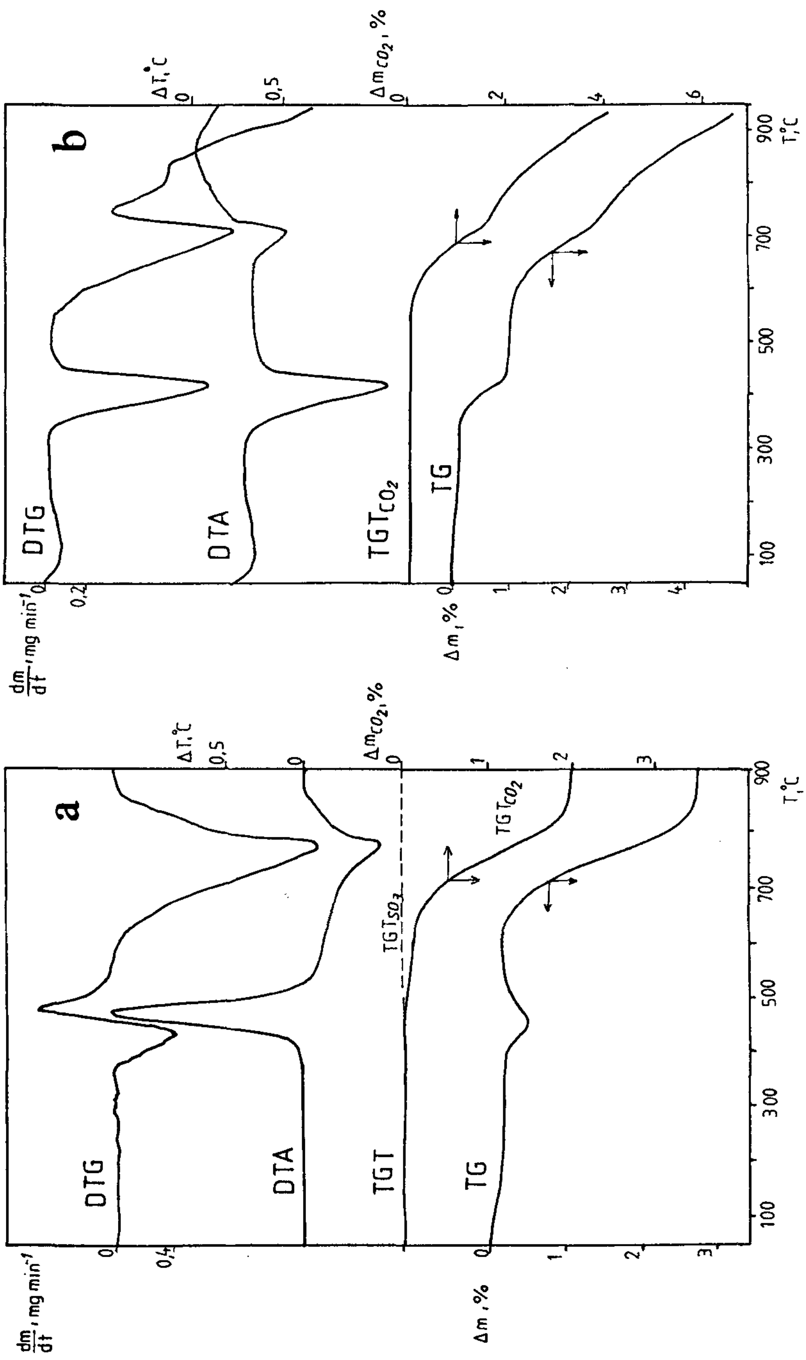

Fig. 2 TG, DTG, DTA and TGT curves for sample 1; a) taken in an oxygen atmosphere; b) taken in a nitrogen atmosphere

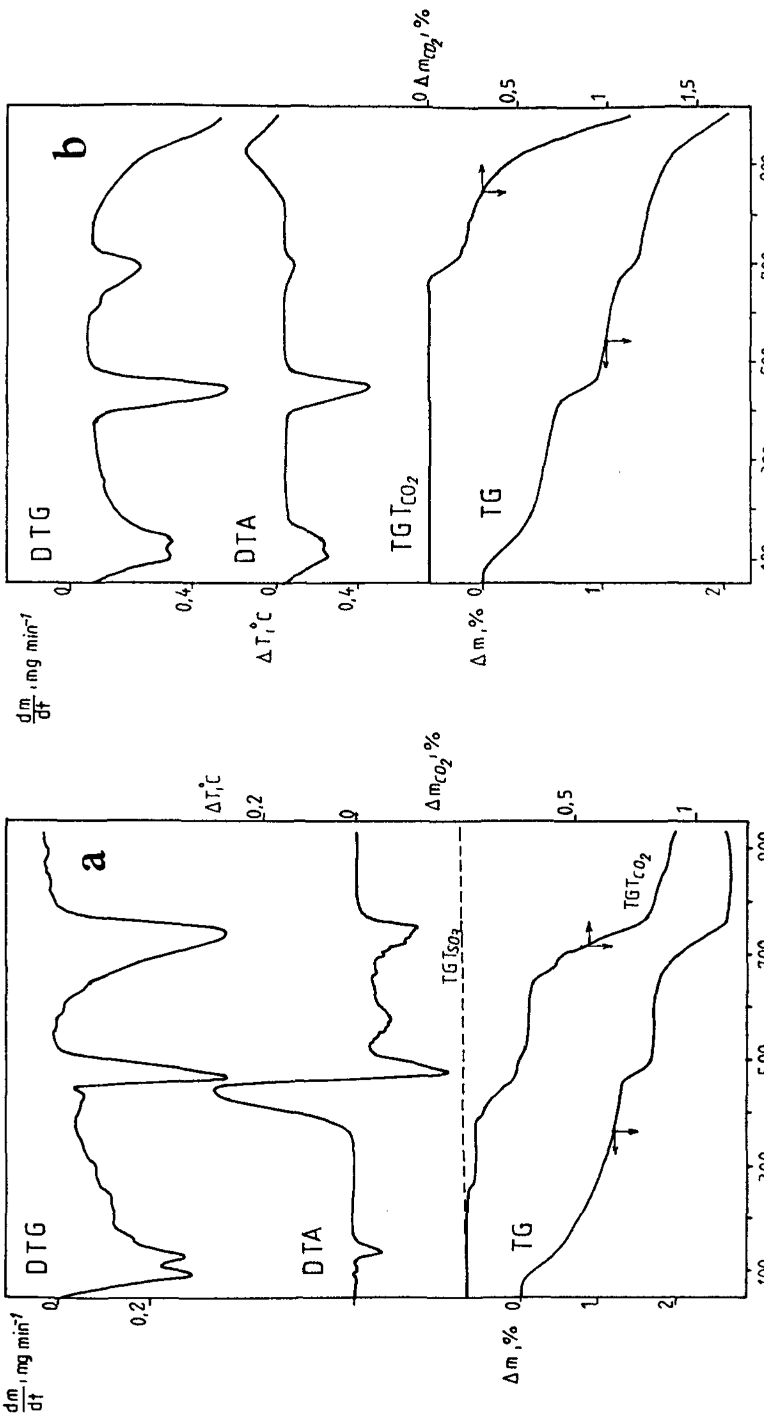

Fig. 3 TG, DTG, DTA and TGT curves for sample 2; a) taken in an oxygen atmosphere; b) taken in a nitrogen atmosphere

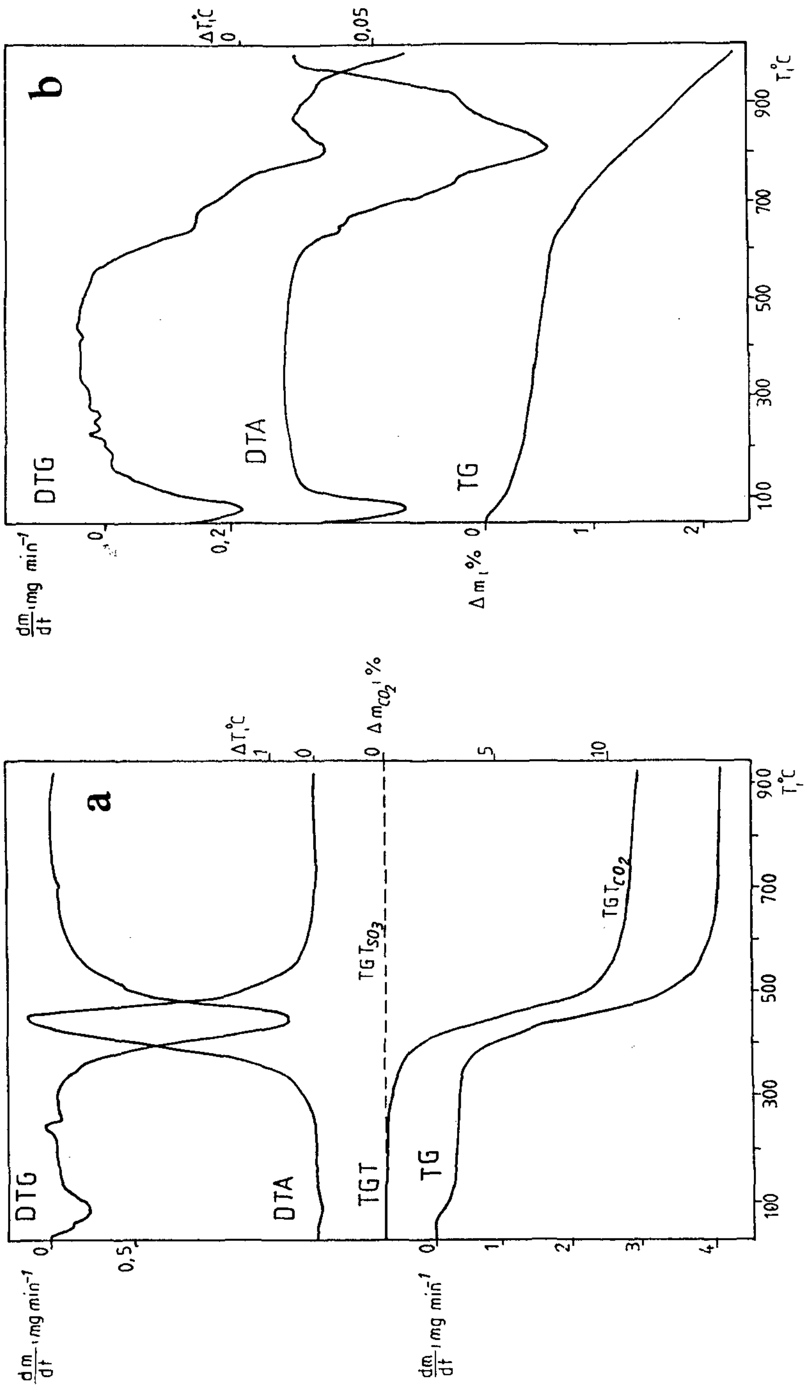

Fig. 4 TG, DTG, DTA and TGT curves for sample 3; a) taken in an oxygen atmosphere; b) taken in a nitrogen atmosphere

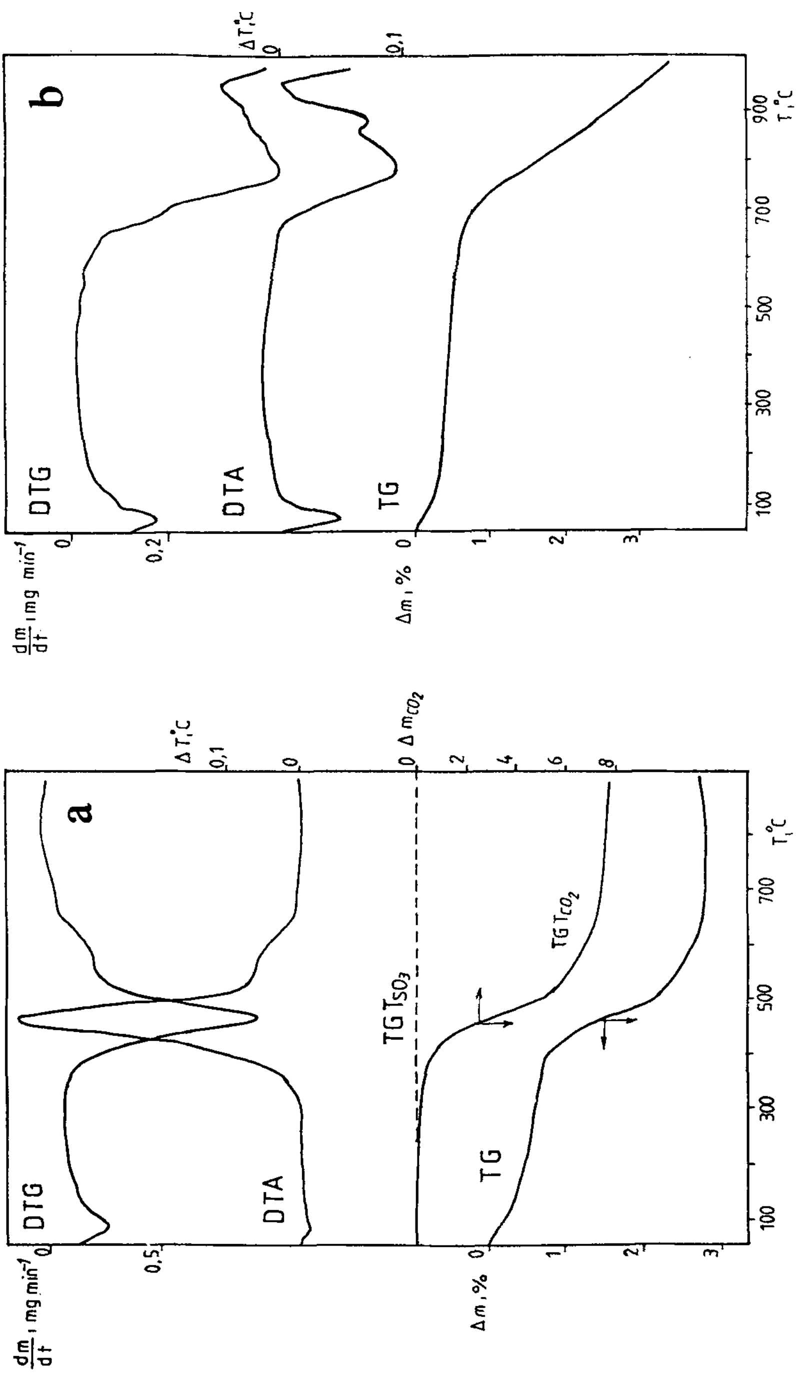

Fig. 5 TG, DTG, DTA and TGT curves for sample 4; a) taken in an oxygen atmosphere; b) taken in a nitrogen atmosphere

processes taking place at about 750°C (Figs 2b and 3b). The original $CaCO_3$ contents of samples 1 and 2 were determined on the basis of the inflection points in the TG and TGT_{CO_2} curves in a nitrogen atmosphere (Figs 2b and 3b), supposing that the total mass loss up to 750°C relates only to the decomposition of $CaCO_3$. The $CaCO_3$ content of sample 1 was about 3.5%, while that of sample 2 was about 0.6%.

It is possible that some of the samples contain sulfurous compounds (e.g. pyrite) besides carbon. These sulfurous compounds give SO_2 and SO_3 in an oxygen atmosphere. In order to determine the carboniferous products and sulfurous compounds in the samples, gastitrimetric measurements were carried out in an oxygen atmosphere at $pH=4.3$ and $pH=9.3$. The titration curves (TGT) are shown in Figs 2a–5a. On gastitrimetry at $pH=4.3$, no SO_3 was found. However, this does not mean that the samples did not contain sulfur compounds which decompose [$Fe_2(SO_4)_3$] or undergo oxidation (FeS) in the measured temperature range. The high CaO contents of the samples (Table 1) can react with SO_3 formed by oxidation, to give $CaSO_4$, which decomposes above 1000°C. Since no NaOH was used for titration of SO_3, the TGT curves at $pH=9.3$ reflect the amount of NaOH consumed for the titration of CO_2.

TGT_{CO_2} curves recorded in an oxygen atmosphere were used for the determination of the carboniferous compounds in the samples. For the samples containing $Ca(OH)_2$ and $CaCO_3$ (samples 1 and 2), for calculation of the carbon contents of the samples, the results of thermogastitrimetric determination of CO_2 were corrected by subtraction of the CO_2 contents of the original samples. The carbon contents of these samples were very low. For sample 1, the TGT_{CO_2} curve in Fig. 2a reveals that NaOH consumption begins only at the temperature where the decomposition of $CaCO_3$ begins, in spite of the fact that an exothermic process takes part at about 450°C. This supports the assumption that the high CaO content of the sample reacts completely with the CO_2 formed by burning. On the basis of the difference in NaOH consumption measured in nitrogen and oxygen atmospheres, the carbon content of the sample was about 0.1%. For sample 2, the TGT_{CO_2} curve shows a two-step process: it begins with the exothermic reaction and proceeds at the temperature where the decomposition of $CaCO_3$ begins. With a correction made on the basis of the TGT_{CO_2} curves recorded in oxygen and nitrogen atmospheres, it was found that sample 2 contained about 0.1% carbon.

As samples 3 and 4 did not contain either $Ca(OH)_2$ or $CaCO_3$, the volume of NaOH used for the titration of CO_2 gave the carbon contents of these samples directly. It was found that the carbon contents in the ashes of lignites were rather high: about 4% for sample 3, and 2% for sample 4.

On the basis of the results of a complete thermal analysis of fly ashes, the burning conditions in the boilers of a power station can be controlled and, if necessary, the burning conditions may be improved.

Finally, it must be emphasized that these results are of only a semiquantitative nature. For a complete analysis of the samples, further investigations are needed, including other experimental methods.

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Zusammenfassung — Mittels simultaner TG-, DTG-, DTA- und EGA-Analyse wurde das thermische Verhalten von Flugaschen aus Elektroabscheidern von verschiedenen kohlestaubbeheizten Warmwasserkesseln untersucht. Mittels Gastitrimetrie wurde der Kohlenstoff- und Schwefelgehalt der Proben bestimmt. Die Zusammensetzung der Proben wurde weiterhin mit Röntgendiffraktion untersucht und mittels klassischer Methoden wurde eine quantitative Oxidanalyse der Aschen durchgeführt.