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TG–DTA–MS INVESTIGATIONS OF COAL, AND CHARACTERIZATION OF THE VOLATILE PRODUCTS RELEASED AS A FUNCTION OF TEMPERATURE

K.-H. Ohrbach, W. Klusmeier and *A. Kettrup**

DEPARTMENT OF APPLIED CHEMISTRY, UNIVERSITY OF PADERBORN, WARBURGER STRASSE 100, D-4790 PADERBORN, GFR.

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Coal samples containing 6.9% volatile matter (anthracite) have been investigated by use of a TG–DTA–MS technique. Estimation of the ash content, volatile matter (d.a.f.) and moisture is possible during one experiment. On running under ASTM conditions, separate tests have to be carried out. When the thermoanalytical curves were recorded in air, a particle diameter of 0.063 mm was most advantageous, because the heating of coal samples with a larger particle size at a heating rate of 10 deg/min^{-1} caused explosion of the particles and the TG–DTA data was not reproducible. The mass fragments of the volatile products range from $m/z = 16$ to $m/z = 300$ at a working pressure of approximately 10^{-6} mbar in the mass spectrometer.

Interest in coal chemistry has grown and become more relevant in recent years. A knowledge of coal structures and the physical properties of coals from different seams will become more important in the future for coal liquefaction and gasifaction of the derived products. The work done in this field has been reviewed by several authors [1, 2]. This is the first occasion that a TG–DTA–MS instrument (thermogravimetry, differential thermal analysis, mass spectrometry) has been used for the analysis of coal samples. Detailed experimental procedures have been described in our previous paper [3–8]. All results discussed in this paper were obtained using a special interface as gas inlet system, reported in [6].

Experimental

A Netzsch STA 429 Thermal Analyzer combined with a Balzers Quadrupole QMG 511 Mass Spectrometer was used to perform investigations on a coal containing 6.9% volatile matter (d.a.f.) in various atmospheres (air, nitrogen, argon, vacuum). Heating rates were varied from 2 deg/min^{-1} to 20 deg/min^{-1}. The DTA sensitivities used were 0.05 mV and 2 mV. The excitation energy in the mass spectrometer was 70 eV. The coal samples were diluted with magnesium oxide before being heated in platinum crucibles.

* Correspondence author

Results and discussion

Investigations of coal samples belonging to different ranks and their characterization by pyrolysis mass spectrometry have been carried out by Meuzelaar et al., and rank-related differences in the mass spectra have been reported [9]. The TG–DTA–MS method described in this paper gives additional information for characterization. A typical weight loss curve with endothermic evolution of moisture, followed by exothermic combustion of the coal in a dynamic air atmosphere in the temperature range 293 K to 1413 K, is shown in Fig. 1.

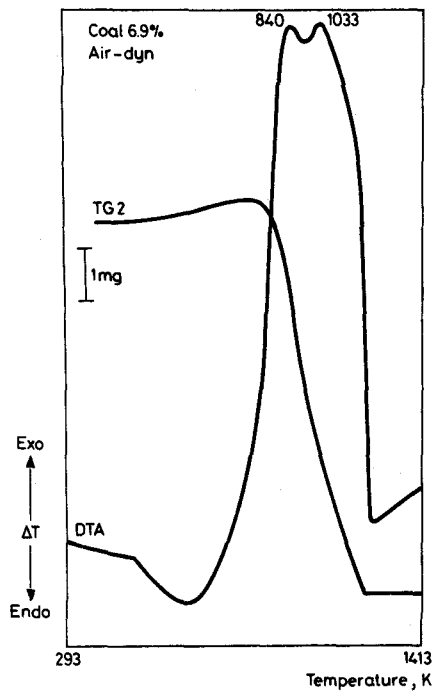

Fig. 1 TG and DTA curves in dynamic air of anthracite containing 6.9% volatile matter (d.a.f.)

This technique offers a direct approach to the study of the thermal behaviour and thermal decomposition reactions of coal when the TG and DTA curves are compared in different atmospheres, i.e. in dynamic nitrogen or oxygen, as shown in Figs 1 and 2.

All experiments described in this paper were performed at a heating rate of 10 deg/min^{-1} with two isothermal sections, first at 623 K and secondly at 923 K, as the example in Fig. 3 shows. This experiment was carried out in vacuum.

The rates of evolution of components are influenced by the heating rate, the isothermal section, dilution materials and occasionally the material of the crucibles,

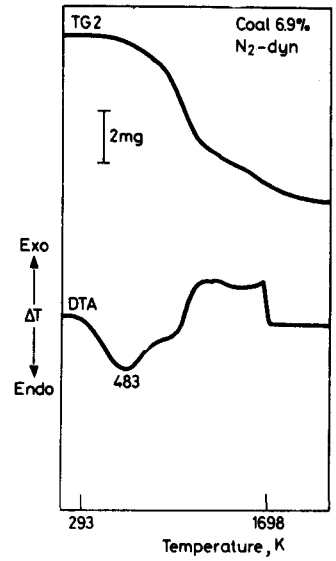

Fig. 2 TG and DTA curves in dynamic nitrogen of anthracite containing 6.9% volatile matter (d.a.f.)

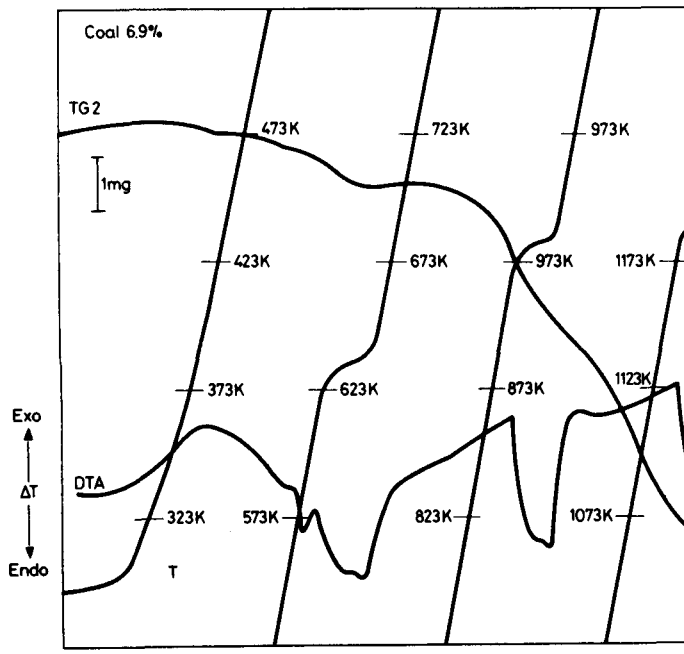

Fig. 3 T–TG–DTA curves of in vacuum ($P = 10^{-5}$ mbar) anthracite containing 6.9% volatile matter (d.a.f.)

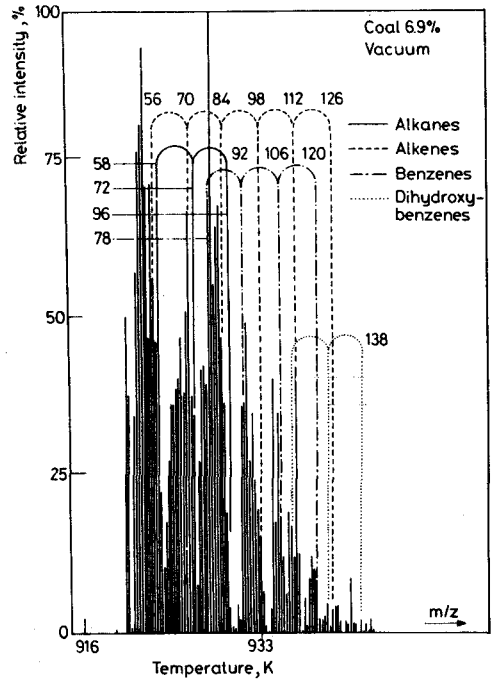

Fig. 4 Mass spectrum in the temperature range from 916 K to 933 K of anthracite containing 6.9% volatile matter (d.a.f.)

when organic products such as coal are investigated. Tests under vacuum (10^{-6} mbar) using platinum crucibles gave the highest yield of volatiles. The compositions of these compounds were quantified with a quadrupole mass spectrometer. Figure 4 is a mass spectrum of the same sample as shown in Figs 1–3, in the temperature range from 916 K to 933 K and in the mass range from $m/z = 45$ to $m/z = 145$.

The mass spectrum in Fig. 4 was scanned at 3 s per mass unit using Al_2O_3 tubes as gas inlet system as described in [6]. It shows the typical fragmentation pattern for hydrocarbons in the above-mentioned mass range for a series of alkanes ($m/z = 44$, 58, 72, 86 . . .), alkanes ($m/z = 56$, 70, 84 . . .), alkylated benzenes ($m/z = 92$, 106, 120 . . .) and alkylated phenols ($m/z = 94$, 108, 122, 136 . . .). An alternative mode of operation for the mass spectrometer allows single ion or mass range monitoring with different scan speeds and sensitivities as a function of temperature, as Fig. 5 shows.

Figure 5 shows the course of different ion currents, corresponding to preselected mass units, which are representative of aliphatic carbons and benzene series. Maxima in the intensities of the ion currents are always accompanied by maxima in the weight loss and the endothermic shape of the DTA curve when data were obtained in vacuum or in an inert gas atmosphere.

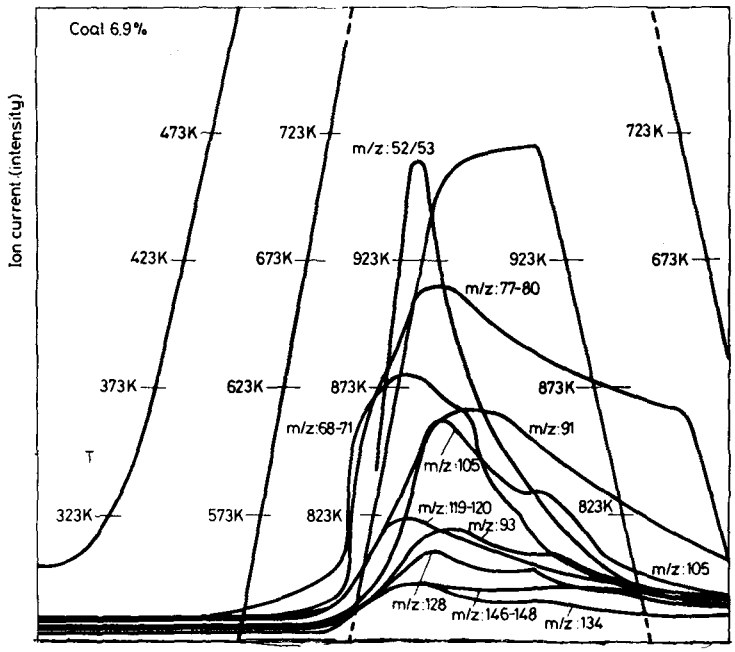

Fig. 5 Mass spectrum (Autocontrol) of selected masses (mass ranges) in the temperature range from 323 K to 923 K

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Zusammenfassung – Kohleproben mit einem Gehalt an flüchtigen Bestandteilen von 6.9% w.a.f. wurden mit Hilfe simultaner Thermogravimetrie-Differenzthermoanalyse-Massenspektroskopie untersucht. Diese Untersuchungsmethode gestattet die Bestimmung des Aschegehaltes, der flüchtigen Bestandteile und der Feuchtigkeit in einem Experiment. Um diese Daten entsprechend der ASTM- (ISO)Bedingungen zu ermitteln, müssen separate Tests durchgeführt werden. Zur Ermittlung der DTA-Daten in Luft unter Normaldruck haben sich Proben mit einem Korndurchmesser von 0.063 mm als vorteilhaft erwiesen. Da durch Anwendung höherer Heizraten als 10 K min^{-1} größere Teilchen explosionsartig zersetzt werden, sind die TG–DTA-Daten nicht mehr reproduzierbar. Die Massenbruchstücke der flüchtigen Bestandteile erstreckt sich von $m/z = 16$ bis $m/z = 300$ bei einem Druck von 10^{-6} mbar im Massenspektrometer.

Резюме – Совмещенным методом ТГ–ДТА–МС были исследованы образцы углей, содержащих 6,9% летучего вещества. Определение зольности, летучего вещества и влаги проводится одним экспериментом. При снятии термоаналитических кривых в атмосфере воздуха, частица с диаметром 0,063 мм была наиболее благоприятной, поскольку нагревание со скоростью 10° в минуту частиц угля с большим размером приводило к взрыву и ТГ–ДТА-данные не были воспроизводимы. Массовые числа летучих продуктов находились в области м/з = 16–300 при рабочем давлении в масс-спектрометре равным приблизительно 10^{-6} мбар.