SIMULTANEOUS THERMAL ANALYSIS–MASS SPECTROMETRIC INVESTIGATIONS OF VOLATILES RELEASED FROM COAL SAMPLES *

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ABSTRACT

This paper deals with the application of simultaneous thermal analysis–mass spectrometry in coal analysis, especially regarding the identification of volatiles released during a temperature controlled program. The analyses have been carried out in dynamic air, in an argon or nitrogen atmosphere and in high vacuum showing the different combustion characteristics by a subtraction method. The evolution profiles of typical structural elements of coal like homologous series of benzene, toluene and xylene isomers, polynuclear aromatic hydrocarbons sulfur dioxide and nitrogen dioxide have been recorded applying different kinds of acquisition modes (analog or computer aided).

INTRODUCTION

The mining and processing of coal is of great importance in the study of fossil energy resources, their use in power stations, in the chemical industry, and environmental aspects of their extraction and use. The standard methods used for investigation and characterization of coal samples have been described in great detail in numerous articles and special literature. Summarized descriptions of new methods of coal analysis, such as infrared, UV, solid-state NMR and computerized maceral analysis are given in the literature as well as an overview of our previous papers on this subject [1–13]. The application of thermal analysis to coal and petroleum and their related products has been reviewed by the authors evaluating 217 references for coal and 174 references for petroleum covering the years from 1980 to 1985 [14–15]. With respect to coal and char gasification as well as catalytic coal combustion and liquefaction of coal and its derived liquids, several studies have been performed by means of combined rapid pyrolysis with separation and detection methods and Fourier transform infrared spectroscopy. The

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

data reported yield useful information about coal structure and also valuable criteria in connection with coal combustion (gasification, devolatilization) kinetics and reactor modeling [16–21].

EXPERIMENTAL

For detailed information concerning the equipment and experimental procedures see refs. 1–11 and others mentioned therein.

RESULTS AND DISCUSSION

The complex nature of coal structure has been investigated by several authors. Models of the molecular structure of coal have been suggested on the basis of methods such as IR, UV, and NMR spectroscopies, X-ray diffraction and mass spectrometry, as well as from the application of petrographic techniques. All proposals which have been made about the structural entities present in coal have been reviewed, leading to the hydrocarbon skeletons discussed in refs. 14–19.

The standard methods of coal investigation include, among many others, the determination of moisture, volatile matter, and ash content. All methods can only be applied separately under thermal treatment of the sample material; thus it can be suggested that thermal analysis might be well suited to determine these data from one experimental run, because nearly all instrumental conditions may be controlled. The application of DSC, DTA and TG analysis to coal samples has been described previously [20–22] and it has been proposed that its application be standardized, in addition to proximate analysis. It is well known that thermal analysis data are influenced not only by the particle size of the coal grains and by the coal composition but also by all possible instrumental settings. Aspects other than sample composition can easily be adjusted as constants or defined as standard conditions by a convention. At this time and for this reason it is very difficult to compare TA results from various experiments with the same sample run under different instrumental conditions. Evaluation of the thermal analysis curves, i.e., the resulting data caused by changing sample composition during thermal treatment in a defined environment, serves as a characterization or identification of coals.

In general no conclusions can be drawn regarding the composition of the organic matter relative to the composition of the volatilization products of the material. This requires the application of combined separation and detection methods such as thermal analysis–gas chromatography and thermal analysis–mass spectrometry. Pyrolysis–gas chromatography–mass spectrometry has been proved very successfully as an investigation method for this purpose [19,20].
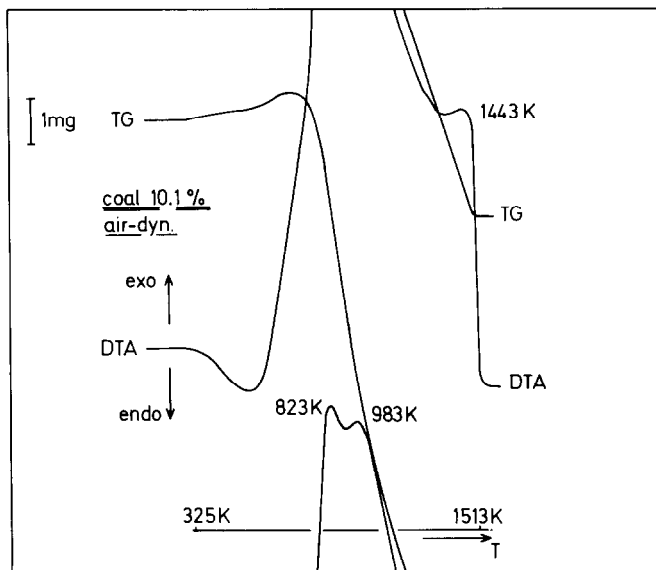
Fig. 1. TA curves of a coal sample in a dynamic air atmosphere.

We have carried out simultaneous TA–MS experiments on coal samples first to prove the usability and applicability of this combined method on coal samples of different grades, ranging from anthracites to high volatile
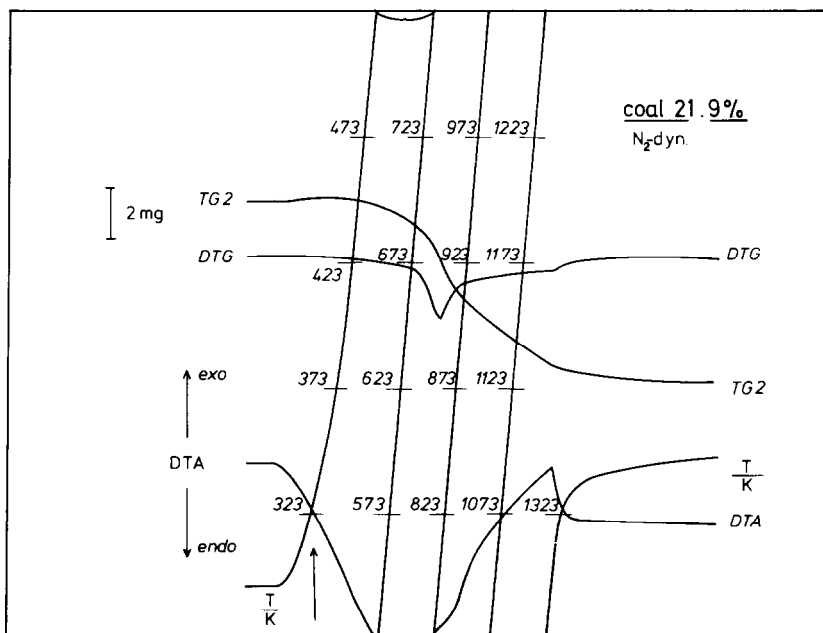

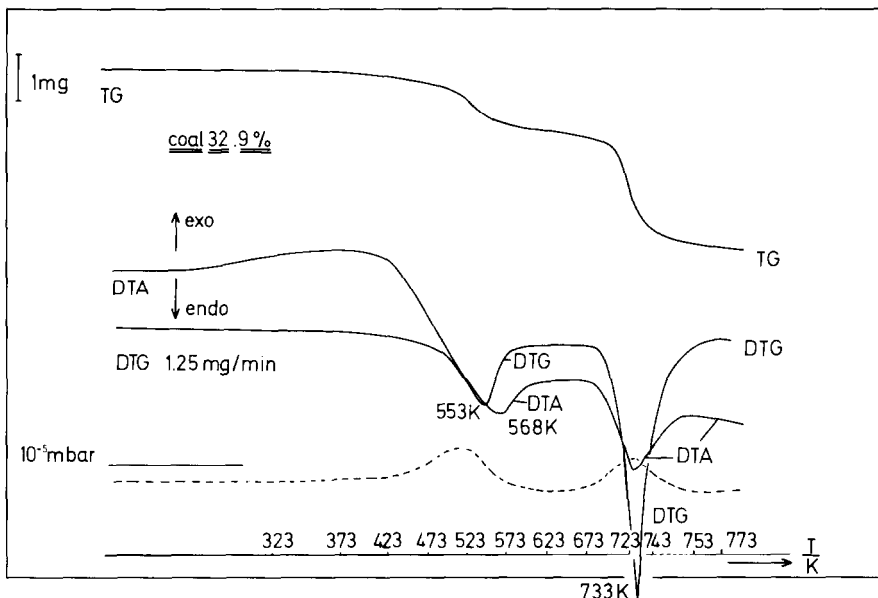Fig. 2. TA curves of a coal sample in dynamic nitrogen.

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Fig. 3. TA curves of a coal sample in high vacuum.

bituminous coals, applying high vacuum at 10^{-3} Pa. The TA curves of a coal containing various amounts of volatile matter, dry and ash-free, are shown in Figs. 1–3.

The reliability of the TA–MS results and the sensitivity of the measuring devices are shown in Fig. 3. The experiment was carried out in high vacuum using a coal sample with 36.3% volatile matter content d.a.f. The evolution of gaseous products from thermal decomposition leads to a corresponding increase of pressure, where the maximum evolution rates correspond to the degradation rates.

The changes in shape and size of the thermal effects taken from the thermoanalytical curves which have been discussed in refs. 4 and 5 are as expected, dependant on the applied atmosphere at constant instrumental settings. Numerous examples show that mass spectra recorded in situ by the use of analog output and two different registration modes yield information about the composition of the volatiles. A typical overall mass spectrum measured for the anthracite sample (see Fig. 3) is demonstrated in Fig. 4 and discussed in ref. 6. A variation of this method is to perform repeated scans of preselected mass fragments of interest as a function of temperature. The increase or decrease of concentration in the gas phase of $m/z = 92$, 77 and 78 a.m.u. in the indicated temperature range is exhibited in Fig. 5. The volatile components released correspond to toluene, phenyl cation and benzene. Another example of the mass spectrometric detection mode leads to the simultaneous temperature-dependant measurement of up to 11 pre-
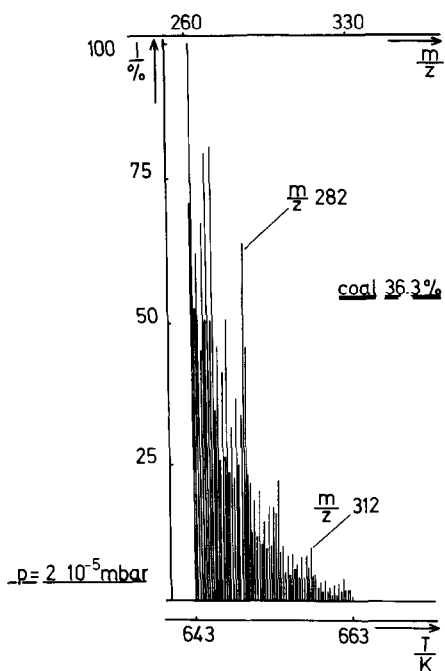
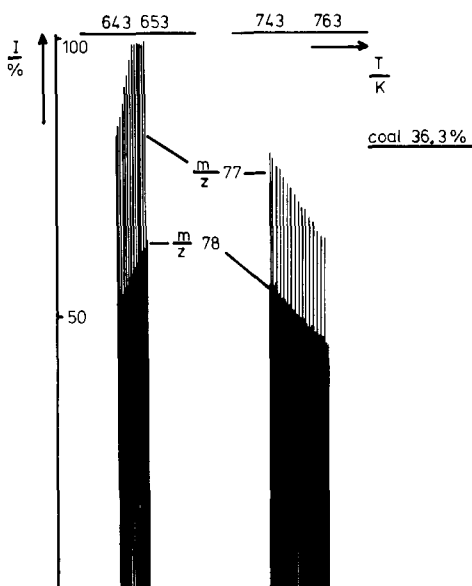Fig. 4. Mass spectrum of a coal sample with 36.3% volatile matter d.a.f.

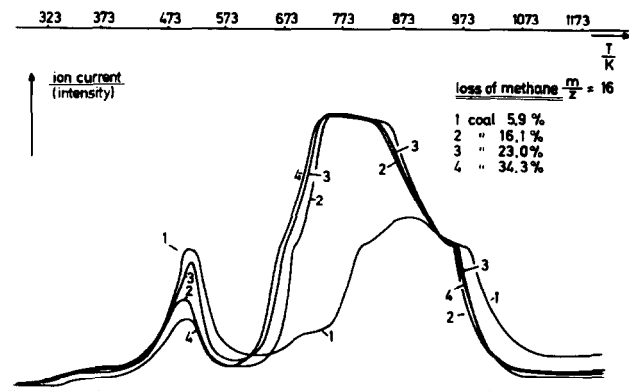Fig. 5. Mass spectra of a coal sample with 36.3% volatile matter d.a.f. in high vacuum.

Fig. 6. Loss of methane from four coal samples (1, 5.9%; 2, 16.1%; 3, 23.0%; 4, 34.4% volatile matter d.a.f.).

selected mass fragments or mass ranges. Each curve shown in the T/intensity plots corresponds with the intensity of the recorded ion currents (see, for example, Fig. 6, the formation of methane from different coal samples taken from four experiments and discussed in ref. 10).

The course of ion current intensities due to the evolution of a series of alkenes, BTX-aromatic (benzene, toluene and xylene isomers) compounds and the phenol series is given in Fig. 7 and discussed in ref. 5. It is well
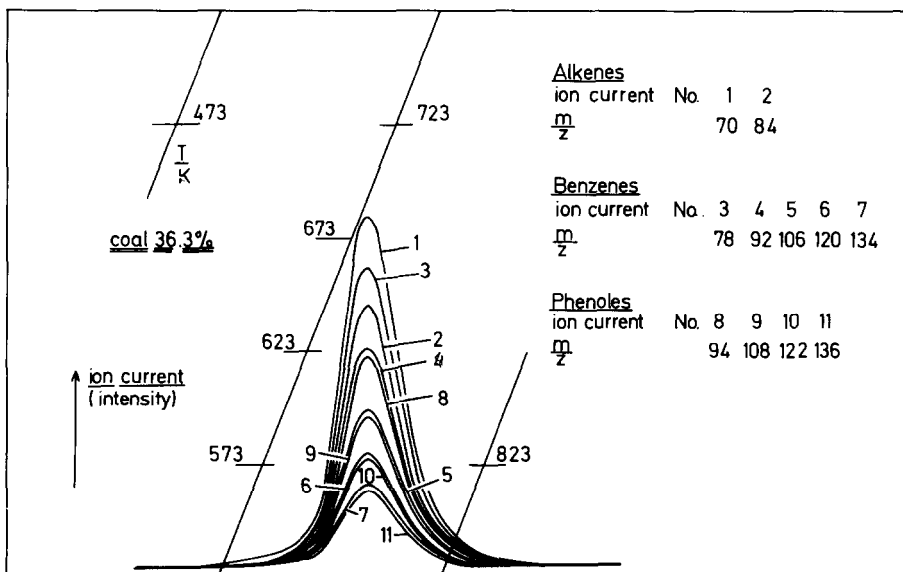

Fig. 7. Course of different ion current intensities corresponding with the indicated m/z values.

known that alkaline earth oxides catalyze the thermal decomposition of organic materials. For this reason we have investigated the thermal degradation of a high volatile bituminous coal as well as its related asphaltene and asphaltole fraction in order to determine the temperature shifts of the characteristic data. Of particular interest are the maximum evolution rates of the gases nitrogen dioxide and sulfur dioxide which are of environmental importance in coal combustion technology. The sample material was diluted with MgO in a 1 : 1 ratio and the TA measurements were made separately in an air and argon atmosphere [11].

In order to determine rapid changes in the composition of the volatiles released and for better data handling and acquisition we coupled the mass spectrometer (Balzers QMG 511) via a commercial interface (Balzers) to a microcomputer (Digital Equipment PDP 11/23 +). The installed operating system of the microcomputer is RT 11 and was compiled with the Fortran IV programming language. The self-developed software package includes means for data acquisition, rapid control of the instrumental settings, storage of data and all evaluation routines of the MS data. It is now possible to record the spectra applying scan speeds of 1 ms per mass unit, i.e., only a few seconds analysis time over the total mass range. The tabulated output of the counts permits statistical evaluation as well as comparison of spectra by a subtraction method which can be shown as hard copy graphically. Each signal or sum of intensities of mass fragments or mass ranges from the overall mass spectra can be plotted versus the temperature. One example is given in Fig. 8. In contrast to the high vacuum operation mode and to the related asphaltene and asphaltole fractions, the highest mass per charge values have been in the range of 130 a.m.u. for the coal sample and 64 a.m.u. in the case of the asphaltenes and asphaltoles.
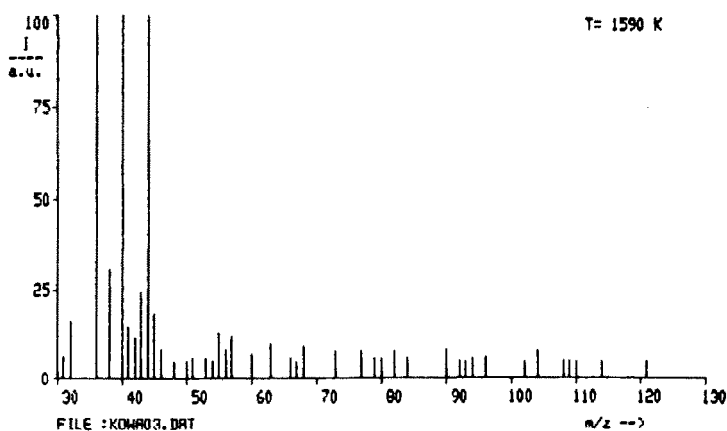

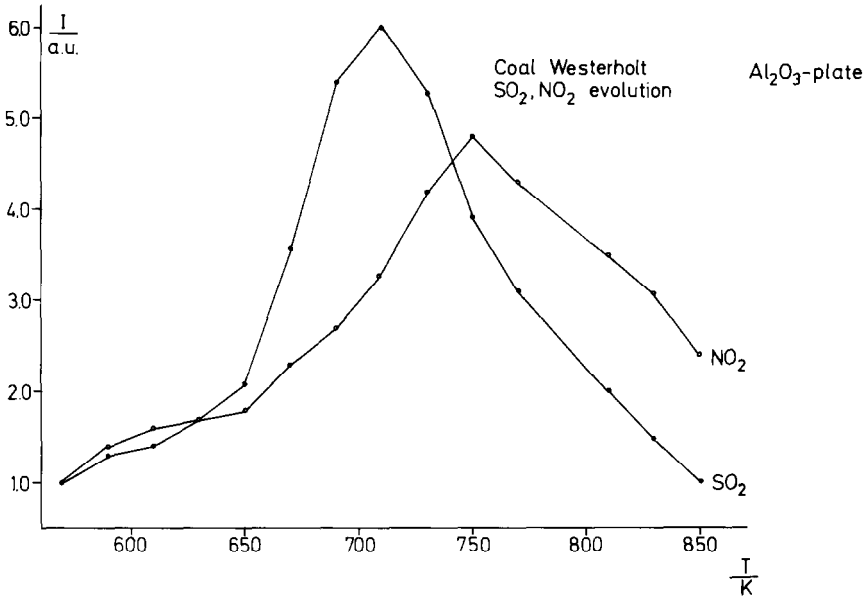Fig. 8. Mass spectrum of Westerholt coal in an argon atmosphere.

Fig. 9. Intensity of the ion current of sulfur dioxide and nitrogen dioxide in air from Westerholt coal.

As mentioned before it is very advantageous to characterize materials by determining their thermal properties in oxidizing media. Some examples are shown in the following figures. The intensities of the ion currents corresponding with sulfur dioxide ($m/z = 64$ a.m.u.) and nitrogen dioxide ($m/z = 46$) of the Westerholt coal, the asphaltenes and the asphaltoles have been taken from the MS-spectra and plotted vs. the temperature (Figs. 9–11).
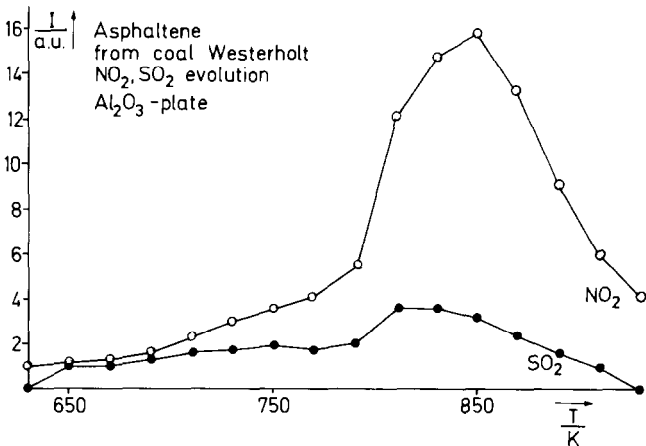

Fig. 10. Intensity of the ion current of sulfur dioxide and nitrogen dioxide from asphaltenes.
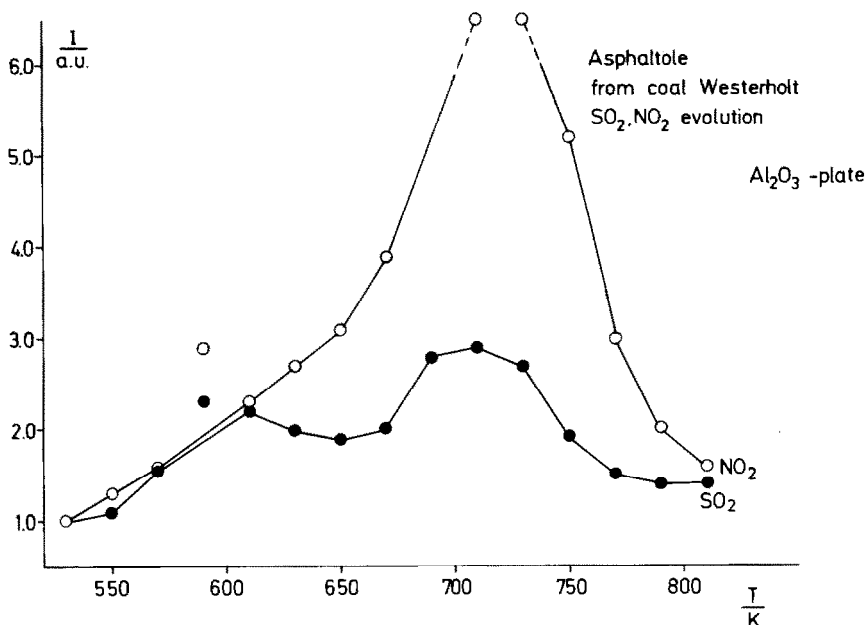
Fig. 11. Intensity of the ion current of sulfur dioxide and nitrogen dioxide from asphaltoles.

These indicate the maximum intensity temperature corresponding with the maximum evolution rates given by the DTG curves. In the cases of MgO dilution of the sample material the sulfur dioxide evolution of all samples occurs in two stages due to the addition of MgO. The second maximum in the curves could not be observed in the indiluted samples, as shown in these examples. These experiments were carried out in an air atmosphere.

CONCLUSION

From our investigations on the thermal decomposition of coal samples and related products it can be concluded that the equipment may be well suited to perform complete on-line control of the coal gasification process, closely simulating process conditions without liquefaction parameters.

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