Thermochimica Acta, 72 (1984) 165—169
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

SIMULTANEOUS THERMOANALYTICAL AND MASS SPECTROMETRIC INVESTIGATIONS OF A GASFLAME COAL

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ABSTRACT

TG-DTG-DTA curves of an exemplary coal with a high volatile matter content of 39,7 % (d.a.f.) have been recorded in vacuum. The composition of the evolved gas was examined by a quadrupole mass spectrometer. Series of aliphatic hydrocarbons, benzenes, anthracenes, naphtalenes and phenols have been detected as a function of temperature. The maxima of the volatile release correspond to thermal effects, shown in the DTA curves and sharp peaks in the DTG curve due to weight loss of the sample, and also correspond to maxima in intensity of selected ion currents registered by the mass spectrometer.

INTRODUCTION

This report is a condensed version of a lecture given by Kettrup (1) about TG-DTG-DTA-MS measurements of coal samples with high volatile matter content on continuing work in the field of simultaneous thermoanalytical and mass spectrometric investigations (2-5). This paper gives another aspect regarding the applicability of the instrumental equipment as evolved gas detection. Combination of very different methods are sometimes accompanied by a loss of sensitivity. In our previous reports (1,2) we have shown by example of an anthracite that the TG-DTG-DTA-MS apparatus is well suited for simultaneous measurements without loss of sensitivity.

0040-6031/84/$03.00

EXPERIMENTAL

Netzsch STA 429 Thermal Analyzer coupled with Balzers Quadrupole Mass Spectrometer QMG 511 was used to carry out our TG-DTG-DTA-MS experiments in vacuum about 10^{-5}mbar. The samples (5-10mg) were diluted with magnesium oxide and heated in platinum crucibles without using the gas inlet system as pressure reduction (6). Experimental conditions have been described elsewhere (2-5).

RESULTS AND DISCUSSION

In contrast to our further investigations in coal samples we examined a gasflame coal (rank Westerholt) with a high volatile matter content of 39,7 % (d.a.f.) and particle size 0,063 mm diameter. The TG-DTG-T and pressure data were recorded simultaneously by a six channel point printer in the temperature range up to 1300 K, see Fig. 1.

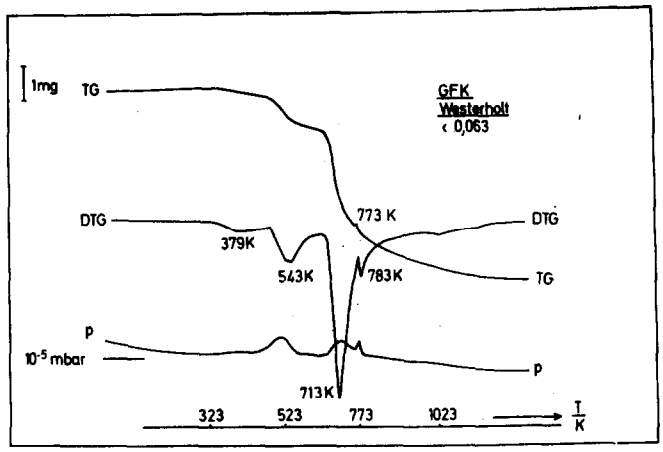

Fig. 1. TG-DTG-T-P curves of a gasflame coal with 39,7 % (d.a.f.) volatile matter content

The effects of weight loss, resulting from evolved gas, indicated in the TG and DTG curves, increase pressure in the mass spectrometer due to loss of water, carbon dioxide and low chain hydrocarbons. The loss of water and carbon dioxide was detected by rapid scans of the single ions of m/z = 18 and m/z = 44, see Fig. 2. In this temperature range shown in Fig. 2 up to 526 K no increase of m/z = 28 (carbon monoxide) has been observed.

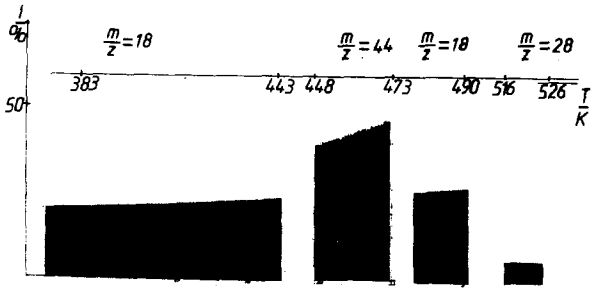

Fig. 2. Detection of water, carbon dioxide and carbon monoxide up to 526 K by scanning the corresponding ions currents m/z = 18, 44 and 28

Another example of rapid scan detection in the mass range from m/z = 77 to m/z = 82, now at constant temperature of 943 K is shown in Fig. 3, with decreasing values for the intensities of the degradation products of the volatile release

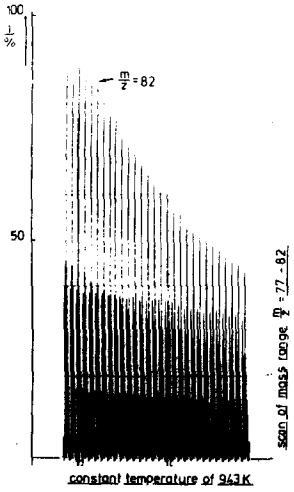

Fig. 3. Rapid scan in the mass range from m/z = 77 to m/z 82 at 943 K

The course of intensities of different series of hydrocarbons is given by the next example in Fig. 4.

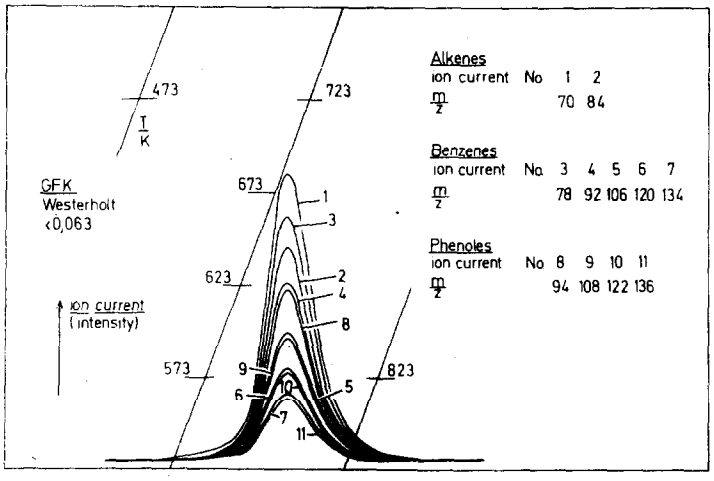

Fig. 4. Course of different ion currents corresponding to m/z values from series of alkenes, alkylated benzenes and phenols

We have chosen eleven mass fragment ions corresponding to hydrocarbon series mentioned above and found maxima intensities for their ion currents at about 690 K at low sensitivity in the mass spectrometer. The same sample was inserted to show the temperature dependent evolution of coal containing compounds in higher mass ranges with high sensitivity in the mass spectrometer, see Fig.5.

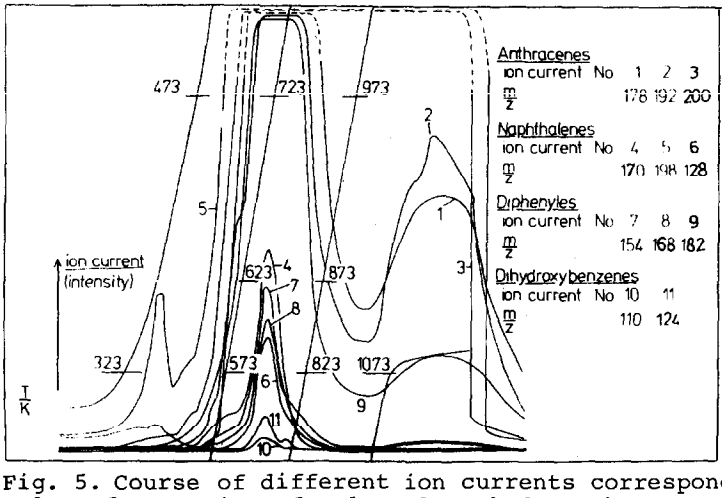

Fig. 5. Course of different ion currents corresponding to m/z values from series of polynuclear hydrocarbons.

Meuzelaar has pointed out by pyrolysis mass spectroscopy of different Rocky Mountains coals that increasing carbonization of the coal increases the concentration of aromatic compounds accompanied by a decrease of aliphatic hydrocarbons content (7). Therefore we have looked for the polynuclear hydrocarbons content of the gasflame coal "Westerholt". The intensities of some ion currents run out of scale range even at lower temperatures and a few derivatives of the antracene series reach a second (third) maximum intensity higher than 1073 K.

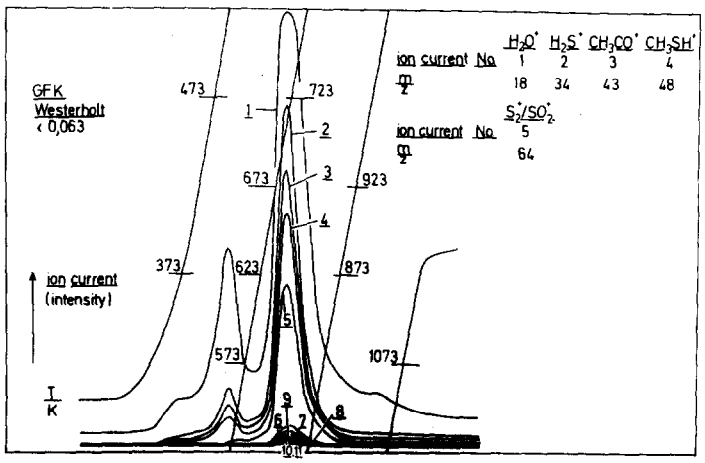

Fig. 6. Course of various ion currents corresponding to m/z values mentioned in Fig. 6.

Running studies of coal samples comming from different ranks with various grade of carbonization aim at a better understanding of coal structure by evaluating the TG-DTA-MS data.

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