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Studies of the yield of sulphur from a coal sample by pyrolysis–gas chromatography

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ABSTRACT

An SBN standard coal 136 (20–100 μg) was pyrolysed in order to characterise the sulphur in coal by Py–GC. The sulphur-containing pyrolysis products were separated and detected by a flame photometric detector. Simultaneously, a flame ionisation detector was used to measure the total amount of organic pyrolysis products.

The influence of different conditions, sample handling, inertness of the system and pyrolysis temperature on the yield of sulphur was tested.

The repeatability was good, even with sample sizes of less than 100 μg. The maximum yield of sulphur was about 40% at pyrolysis temperatures of between 1000 and 1400°C. When the coal samples were combusted after pyrolysis, an additional 30% was detected. The reason for the low yield is discussed.

Coal; FID; FPD; Py–GC; pyrolysis; sulphur.

INTRODUCTION

During the years several attempts to fully characterise coal have been made. Many different techniques and methods have been used [1]. Owing to the heterogeneity and the diversity in the composition of coal great difficulties have arisen.

Many standardised methods have been established [2]; examples include methods for the determination of the total amount of sulphur, the amount of pyrite and the amount of sulphate, but not for the amount of organic sulphur. The quantity of organic sulphur is determined as the difference between the total amount of sulphur and the amounts of pyrite and sulphate [3]. There are reasons to question the reliability of the sulphur determinations [4].

The sulphur content in coal is of particular interest today since it contributes to the pollution of the environment. Great efforts are made to find new techniques to purify coal, especially from organic sulphur in the

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coal structure, before combustion for energy production [5]. There is still no method that can give qualitative and quantitative information in a simple way about how the sulphur is bound. Pyrolysis–gas chromatography (Py–GC) has been suggested as a feasible technique for the detailed chemical characterisation of coal [6,7]. It has already been used for the quantitative determination of sulphur-containing products; the yield did not reach 100% [8,9]. The aim of this investigation is to clarify the influence of different experimental conditions on the yield and to find experimental conditions leading to a better yield.

EXPERIMENTAL

Apparatus

In Fig. 1 a schematic of the Pyrola filament pulse pyrolyser and the gas chromatograph is shown. The Pt-filament (15 × 2.6 × 0.012 mm) with a cavity for solid samples is heated with two curent pulses [10]. The proper amplitudes of the current pulses, to reach the pyrolysis temperature in a fixed temperature rise time, are chosen by a program in the software of the pyrolyser. It is important to change the amplitude of the current pulses when a new filament is introduced, when a change in chamber temperature occurs, and when the carrier gas flow or gas type are varied [11]. Around the filament is a glass cell to protect the GC-system from non-volatile pyrolysis products. The products which have condensed on the glass walls are removed using a Bunsen flame. The glass cell allows the light to pass to the fibre optic cable from the middle of the filament where the sample is placed, and further on to the photodiode. It is possible to study the temperature time profile (TTP) in detail. In this study the temperature rise time was 8 ms. The resistance of the Pt-filament is used for the measurement

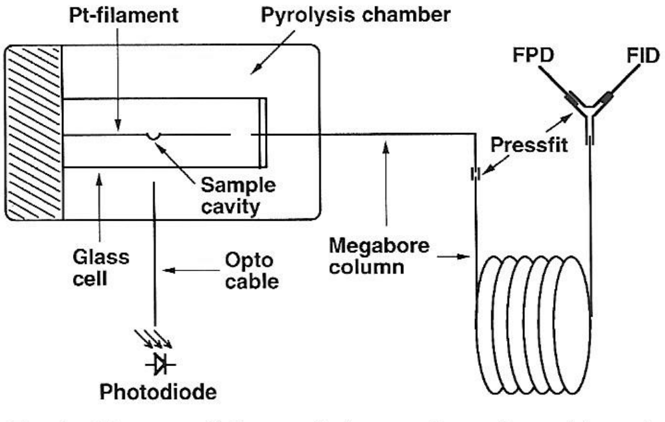

Fig. 1. Diagram of the pyrolysis–gas chromatographic system; FPD = flame photometric detector; FID = flame ionization detector.

of the pyrolysis temperature at low temperatures, less then about 550°C, at which the photodiode is not sensitive. Experiments were done using a glass cell silylated with 5% dichlorodimethylsiloxane in toluene, and with a quartz cell instead of the glass cell.

In general, the connection between the pyrolysis chamber and the GC-column was made with a short length of GC-column. A metal tube to the GC-injector was used in one set of experiments. The outlet of the column was split to two detectors, a flame ionization detector (FID) and a flame photometric detector (FPD).

Combustion of the pyrolysis residue was done by substituting the normal helium carrier gas with oxygen. Since the heat transfer is less in oxygen than in helium, the Pt-filament had to be recalibrated with respect to the current pulses [11].

The experimental conditions are given in Table 1.

Samples and sample handling

The ten standard coal samples used in this study came from the European Centre for Coal Specimens SBN, the Netherlands. Their characteristics are presented in Table 2. The particle size was $< 200\ \mu m$ and the sample size was $20-100\ \mu g$.

Coal 136 was pyrolysed and combusted to find the optimum conditions to obtain the maximum yield of sulphur. The sample was placed on the Pt-filament either as a water and ethanol (9:1), or as a glycerol and water (9:1) suspension. The suspending medium was evaporated before pyrolysis. The sample was positioned directly onto the Pt-filament with a solid sample dispenser, see Fig. 2. The volume of the sample could be varied. The glass micro pipette was filled up to the plunger with the coal sample. The coal sample was then pushed out of the glass micro pipette with the plunger into the cavity of the Pt-filament.

The mass of coal in a certain volume of suspension and of coal from the solid sample dispenser was determined. The suspending medium was first evaporated before weighing. This determination was made for all ten coals.

Calibration

When the calibration was obtained, the pyrolysis probe was substituted with a calibration probe, similar to the pyrolysis probe but equipped with a septum instead of the Pt-filament. Calibration curves for the five most abundant sulphur-containing pyrolysis products were made by injecting different volumes of known concentrations of the gaseous samples, H_2S, COS, MeSH and SO_2, with gas-tight syringes and of a solution of CS_2 in heptane. The gases were obtained from AGA GAS, Sweden, and delivered in pressurised flasks diluted with nitrogen.

TABLE 1

Apparatus and conditions

Apparatus	Model	Conditions	
Pyrolyser	PYROLA Pyrolab Sweden	Temperature rise time:	8 ms
		Pyrolysis time:	2 s
		Pyrolysis temperature:	Variable, see Figs. and Tables
		Chamber temperature:	150°C
Gas chromatograph	Vista 6000 Varian USA	Detector:	FID (attn. 1×10^{-10}) and FPD (attn. 1×10^{-8})
		Detector temperature:	250°C
		Injector temperature	250°C
		Carrier gas:	He, 20 ml/min
		Column:	DB-1 (J&W), 3 μm, 30 m, 0.52 mm ID
		Column temperature:	-50°C (1 min) $\rightarrow$ (15°C/min) $\rightarrow$ 250°C (2 min)
Integrator software	Baseline Waters USA		

TABLE 2

Characteristics of the different SBN standard coals

Coal sample*	% weight					
	Volatile matter	Carbon	Pyritic S	Sulphate S	Organic S	Total S
101	7.33	85.23	0.77	0.04	1.01	1.82
126	31.64	71.60	0.54	0.22	0.17	0.93
129	20.80	75.12	0.45	0.52	1.13	2.10
134	4.50	92.16	0.01	0.01	0.58	0.60
136	44.99	60.15	1.13	0.06	3.86	5.05
141	9.67	72.77	1.85	0.58	0.11	2.54
162	42.70	79.50	0.01	0.00	0.40	0.41
171	30.12	72.41	0.03	0.07	0.73	0.83
177	32.80	69.40	0.87	0.05	0.46	1.35
501	27.11	64.89	0.76	0.93	0.77	2.46

* Dry base.

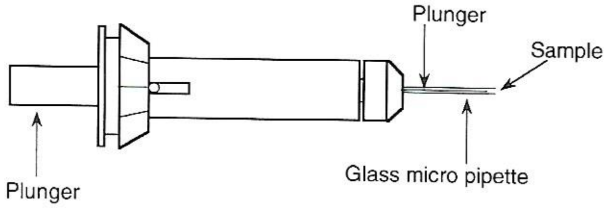

Fig. 2. Solid sample dispenser used for the application of coal samples.

RESULTS AND DISCUSSION

Pyrolysis products

In this study we have concentrated on the results from the FPD and only used the sum of the peak areas from the FID in the experiments presented in Fig. 3. A pyrogram showing the sulphur-containing pyrolysis products when coal 136 was pyrolysed at 800°C for 2 s is shown in Fig. 4. Although 76% of the sulphur in coal 136 is organic, the most abundant products obtained by pyrolysis were inorganic. We expected to find more thiophenes, as they are the most stable sulphur products and are supposed to be the major constituents of the organic sulphur content [12]; however, the results are in agreement with those presented in the literature [9,13].

Repeatability and reproducibility

In order to be able to determine the differences in the yields of the sulphur-containing products when changing the experimental conditions, it

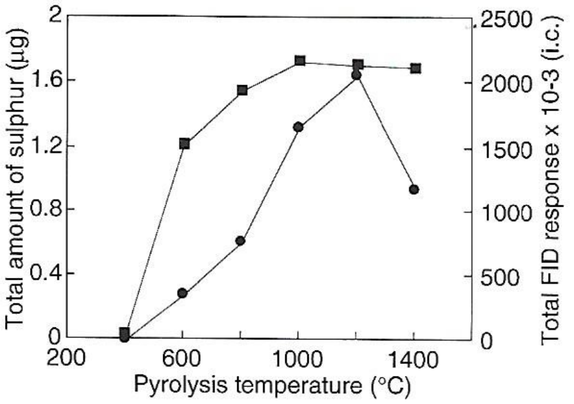

Fig. 3. Total amount of sulphur (■) and total FID response (●) obtained when coal 136 (100 μg) was pyrolysed at different temperatures for 2 s.

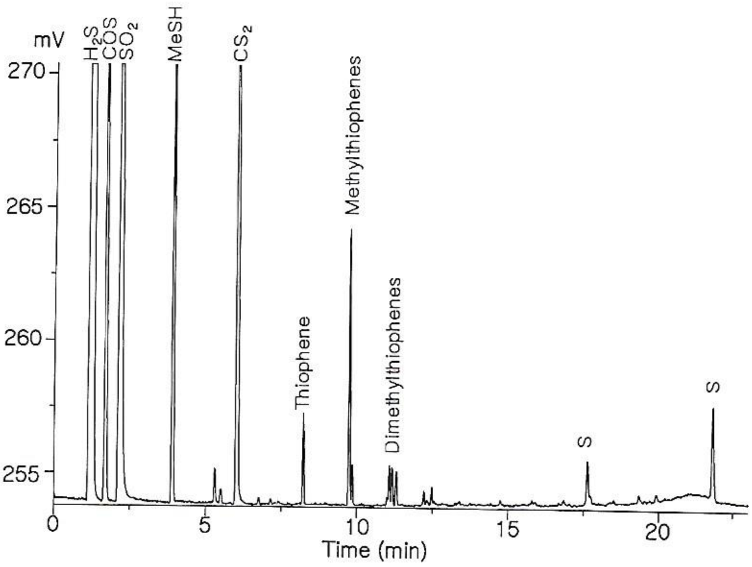

Fig. 4. Pyrogram of coal 136 (100 μg) pyrolysed at 800°C for 2 s; S = elemental sulphur [7].

is necessary to obtain reproducible results. The positioning of a known amount of the sample onto the Pt-filament must be reproducible.

The mass of the ten coals in the water and ethanol suspension ($n = 3$) and the mass of the ten coals applied by the solid sample dispenser ($n = 5$) were determined. The results are shown in Table 3. The masses should have been 100 μg. For the suspensions the masses varied between 74 and 123 μg, and for the solid samples between 87 and 106 μg. The differences in the masses of the coals could be explained by different particle sizes, densities and content of volatile matter. The repeatability of sample application was better when the sample was applied as a solid compared to when the sample

TABLE 3

Repeatability of the masses of SBN standard coals in suspension and as solid sample

Coal sample	Suspension		Solid sample	
	Mass (μg), $n = 3$	RSD (%)	Mass (μg), $n = 5$	RSD (%)
101	74	2	95	2
126	102	15	93	2
129	104	20	89	4
134	89	12	106	4
136	104	20	104	1
141	123	4	106	3
162	113	5	87	2
171	98	5	98	1
177	121	9	99	3
501	97	3	101	3

n = number of measurements

was applied as a suspension. This might depend on experimental errors, because of difficulties in volatilising the water before weighing the samples rather than actual differences in the masses of coal.

A glycerol and water (9:1) suspension was also tested in order to keep the suspension more stable because of the higher viscosity. There were difficulties in evaporating the glycerol and, thus, it was not possible to check the amount of sample actually pyrolysed. The information from the FID was sometimes misleading. The glycerol was not totally evaporated before pyrolysis and, thus, contributed to the total amount of organic products.

Coal 136 was pyrolysed at 1000°C and the result are shown in Table 4. The amounts of sulphur in the five main sulphur-containing pyrolysis products were determined. S_{tot} represents the sum of sulphur in these five products. The two different sample handling techniques are compared. The repeatability was good except for SO_2 for both techniques. However, the solid sample technique made the sample handling and the checking of the actual mass pyrolysed easier.

The repeatability of the pyrolysis results was also determined using the same column (A), column A one month before when it was quite new (B), and another column (C), which had been used for a long time but had the same characteristics. All other conditions were the same. The results, which are shown in Table 4, give information about the reproducibility of the whole system.

Influence of instrumental design

Preliminary experiments were carried out to see if the material in the connection between the pyrolysis chamber and the column influenced the

TABLE 4

Distribution and repeatability of sulphur in the pyrolysis products from Coal 136 pyrolysed at 1000°C for 2 s under three different circumstances: when a relatively new (A), a brand new (B) and an old GC column (C) were used, for the separation ($n = 3$)

Column	Coal 136	H_2S		COS		SO_2		CH_3SH		CS_2		S_{tot}	
		Solid	Susp*	Solid	Susp*	Solid	Susp.*	Solid	Susp*	Solid	Susp*	Solid	Susp*
A	1	10.6	9.7	0.47	0.25	1.4	1.2	0.40	0.27	3.0	1.7	15.8	13.1
A	2	10.9	9.7	0.48	0.26	1.5	0.9	0.42	0.25	3.0	2.2	16.3	13.3
A	3	10.6	8.9	0.45	0.30	2.2	1.2	0.45	0.25	2.8	2.4	16.5	13.0
A	Mean**	10.7	9.4	0.47	0.27	1.7	1.1	0.42	0.26	3.0	2.1	16.2	13.1
	RSD(%)	2	5	4	9	26	16	6	5	3	16	2	1
B	Mean**	11.0		0.47		3.0		0.38		3.6		18.4	
	RSD(%)	1		4		6		3		3		2	
C	Mean**	11.3		0.48		0.96		0.38		2.8		16.0	
	RSD(%)	1		8		6		11		10		4	

* Water and ethanol suspension.

** $n = 3$, values in ng S/μg coal.

yield of sulphur-containing pyrolysis products. The results when a metal was used were compared with those from the inert system when a piece of the GC-column was used. The same pyrolyses were done using two different pyrolysers of the same brand. The same column and detector system were used. The amount of sulphur-containing products formed when the metal was present was less, but no drastic change was noticed. However, the distribution of products was nearly the same, which might explain that the decrease can depend on factors other than the influence of metal.

The glass cell was changed to a quartz cell, in order to investigate the effect of active sites in the glass cell, which were expected to be more abundant in the borosilicate glass that is standard in the apparatus. No significant influence on the results was observed when the quartz cell was utilised. Not even SO_2 was influenced by the change in cell material. This might be due to the poor reproducibility of this peak, masking any effect from the change in cells. The same result as above was obtained when the silylated cell was used. An advantage of the silylated cell was that the removal of tar, condensed on the inner walls of the cell during pyrolysis to an extent roughly dependent on the temperature and volatile matter, was simplified and no longer required extensive treatment in a Bunsen flame.

It is important to know the TTP of the pyrolyser and of the sample. Ideally, the TTP is the only parameter that should influence the result of the thermal degradation. In Fig. 5 the first 500 ms of the TTPs, with and without sample, were plotted. The pyrolysis temperature was 800°C and the pyrolysis time two seconds. The decrease in temperature when a sample was pyrolysed depended on the consumption of energy when the coal sample was heated to the temperature of the filament [14], and partly on the endothermal reactions when the coal was thermally degraded.

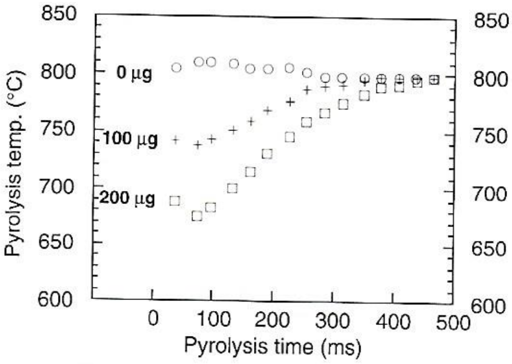

Fig. 5. Three temperature time profiles obtained without sample, and with 100 μg and 200 μg of coal 136, when the Pt-filament was heated to 800°C in 8 ms and kept at that temperature for 2 s.

Influence of the pyrolysis temperature

Coal 136 was pyrolysed at different temperatures for 2 s in order to optimise the yield of the sulphur-containing products (see Fig. 3). The total amount of sulphur increased as the temperature increased to 1000°C and then stayed at the same level. The total amount of organic products measured by the FID decreased above 1200°C, which was due to carbonization. This means that the hydrocarbons are secondarily degraded to carbon and hydrogen [10]. The slow increase in the amount of hydrocarbons with increasing pyrolysis temperature is due to slow reaction rates at very low temperatures, at which most of the hydrocarbons are not released from the coal sample. At higher temperatures the degradation takes place and relatively high boiling products are formed, which can condense on the glass walls as tar. The higher the pyrolysis temperature the more time the tar will have to be further thermally degraded before it leaves the char and, thus, the more products that can pass the GC-system. It is interesting to notice that the amount of the sulphur-containing products increases faster with increasing pyrolysis temperature than that of the hydrocarbons. The most probable reason is that the increase of sulphur originates from the inorganic sulphur in the coal. Pyrite, for example, decomposes at 500–600°C and the free sulphur reacts with hydrogen to form hydrogen sulphide [8].

Influence of the column

The SO_2 peak tended to tail off when an aging column was used, which influenced the yield of the SO_2 (see Table 4). In Fig. 6, the yield of sulphur from H_2S, SO_2 and CS_2, and the sum of the five most abundant peaks obtained from the new and the old column, are plotted. The biggest difference between the two columns is seen at 1000°C. The repeatability of

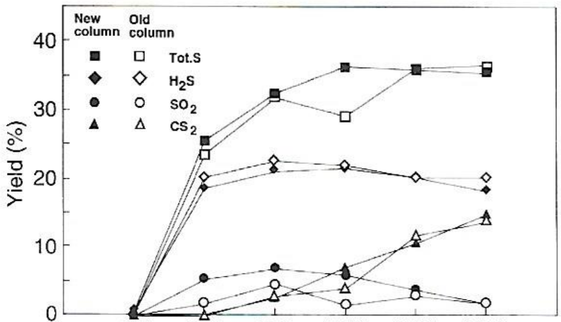

Fig. 6. Total yield of sulphur from coal 136, in per cent of its given value plotted against the pyrolysis temperature for the total sulphur, H_2S, SO_2 and CS_2 obtained. The results were obtained on two different occasions, with a new and an old column respectively.

the sum of the sulphur for the new and the old column ($n = 3$) is 1.5 and 3.8% respectively and, thus, does not contribute to the big difference. The yield of H_2S is the same, but the SO_2 and CS_2 yields are much lower for the old column.

Yield of sulphur

The yield of sulphur for the five first peaks never reached 40% (see Fig. 6). The sulfur in the other peaks, containing organic sulphur products, was estimated at 5%. After each pyrolysis the residue of the coal was combusted in oxygen at 1350°C in order to release sulphur in the char. This increased the yield up to 65% (see Fig. 7). The maximum total yield of sulphur was 70%.

It was possible with the solid sample dispenser to apply masses of coal down to 20 μg. The repeatability of the yield was relatively good. For the sample size 65 μg the RSD was 4% ($n = 3$). The yield increased with decreasing sample size (see Fig. 8) when coal 136 was pyrolysed at 800°C

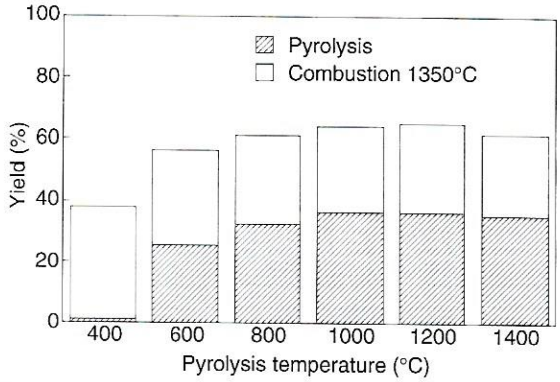

Fig. 7. Total yield of sulphur in per cent of the value obtained when coal 136 (100 μg) was pyrolysed at different temperatures. The residue was combusted at 1350°C after each pyrolysis.

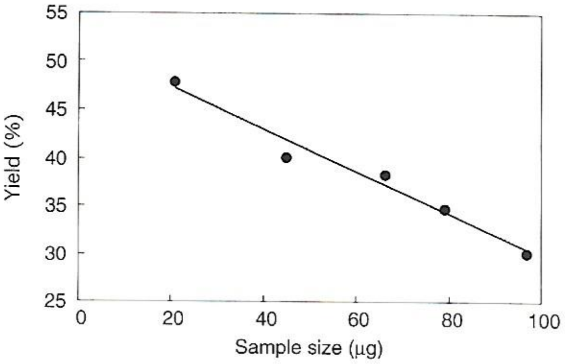

Fig. 8. Total yield of sulphur obtained when different amounts of coal 136 were pyrolysed at 800°C and applied as solids.

for 2 s. This was due to a higher temperature in the bulk of the small sample sizes. In Fig. 6 the influence of pyrolysis temperature can be followed for 100 μg of coal 136. More experiments will be done with sample sizes lower than 100 μg. Pyrolysis will then be followed by combustion of the residue.

CONCLUSIONS

It was possible to apply known and small amounts of coal samples in a reproducible way, which was proved experimentally by weighing and pyrolysing the coal samples.

The total yield of sulphur increased by combusting the residue of the coal after pyrolysis. However, the yield never exceeded 70%.

Systematic errors contributing to this yield of less than 100% included:
(i) problems in obtaining the calibration curves;
(ii) adsorption effects in the system;
(iii) formation of SO_3 which is difficult to detect;
(iv) the lack of precision of sulphur determination in the standard coal samples, which contributes to (iii).

ACKNOWLEDGEMENTS

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