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New approach to the characterization of pyrolysis coal products by gas chromatography–mass spectrometry

Achille Cappiello^{a,*}, Filippo Mangani^a, Fabrizio Bruner^a, Loretta Bonfanti^b

^a*Istituto di Scienze Chimiche, Università di Urbino, Piazza Rinascimento 6, 61029 Urbino, Italy*

^b*ENEL, Thermal Research Center, Via Andrea Pisano 120, 56100 Pisa, Italy*

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Abstract

A method for the characterization of coal thermal behaviour, based on gas chromatographic–mass spectrometric analysis of the pyrolysate, is presented. Twelve different coal samples, representative of the entire coal rank, were selected for this study. The pyrolysis products, obtained at 800°C, were first collected and then analysed in two GC–MS systems. The sampling apparatus consisted of three different traps in order to separate the products into three fractions on the basis of their volatility. The GC–MS analysis was also arranged according to this criterion. A packed column, coupled to a double-focusing magnetic mass spectrometer, was used for the volatile fractions of the pyrolysate and a capillary column, coupled to a quadrupole analyser, was employed for the analysis of the condensed fraction. Sampling and analysis procedures were carried out separately, thus allowing careful optimization of the strategy for the characterization of the pyrolysate. The condensate was analysed in the selected-ion monitoring mode for the determination of different classes of compounds. Some evaluations and comparisons, extrapolated from the results obtained, are presented.

Keywords: Coal; Alkanes; Phenols; Polynuclear aromatic hydrocarbons; Benzene; Toluene

1. Introduction

Coal is a heterogeneous and structurally complex material consisting of a large number of organic and inorganic compounds. It is mainly used as an energy resource and as a raw material for the production of chemicals. Coal is found and extracted in many different locations and its structure and composition record the geological history through which it was generated. Moreover, the composition of coal and its structure

influence the combustion efficiency. Global environmental concerns require a careful examination of all steps involved in energy production, in the light of the fact that the emission of several pollutants appears to be linked to certain precursors originally present in the fuel. For all these reasons, coal characterization is a source of valuable information.

The characterization of coal is a very complex matter and must take account of several aspects of its nature. Hence a large number of standard analyses and tests have been developed [1,2]. Examples of conventional standard coal charac-

* Corresponding author.

terization methods are proximate analysis (moisture, ash, volatile matter and fixed carbon content), elemental analysis (C, H, N, S and O content), petrographic analysis, calorific value and swelling index. On the basis of these methods, coals are classified according to a rank order. With increasing coal rank, coals are assigned to one of the following classes: peat, lignite, sub-bituminous coal, bituminous coal, anthracite and graphite.

More recently, the availability of modern investigation techniques have oriented coal characterization towards different strategies: electron spin resonance spectroscopy (ESR) [3], solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy [4–6], Fourier transform infrared (FTIR) spectroscopy [7,8] and Curie-point pyrolysis techniques [9,10]. Modern analytical strategies can provide a deeper and more accurate picture of the detailed coal composition.

A knowledge of coal behaviour under pyrolytic conditions is important for coal characterization. Pyrolysis is involved in several coal manipulations such as hydrogenation, gasification and liquefaction, influencing both process efficiency and product quality [11,12]. Therefore, the investigation of coal thermal behaviour can be considered a basic topic in coal characterization studies [13–15].

A reliable technique particularly suitable for this application is on-line pyrolysis–GC or GC–MS with cryogenic cooling [16–19]. This simple approach consists of a sample heating step followed by condensation of the pyrolysate into a capillary cooled by liquid nitrogen. The capillary is subsequently connected to a GC system for compound separation. A limitation with this procedure is that, owing to the very complex matrix, a large number of different compounds, with different volatility and polarity, are involved in the same identification process. This paper suggests a novel approach to coal characterization based on accurate and reliable analyses of the pyrolysis products. In this method, the sampling procedure is chronologically and physically separated from the analytical procedure. Particularly attention was devoted to improving both steps of the overall analytical process. The pyrolysis

products were first collected, on the basis of their volatility, in three different traps and then analysed, by GC–MS, following the same criteria. GC and MS analyses were carried out on the basis of the chemical properties of the different fractions collected. Owing to an intrinsic limitation, only the heaviest part of the pyrolysate was not considered in this study and its analysis will be better accomplished by liquid chromatography (LC)–MS. Our investigation was restricted to some well defined classes of compounds in order to suggest some possible strategies for the characterization of coals. On the basis of the results obtained, some correlations are outlined and discussed.

2. Experimental

2.1. Sampling apparatus

Coal samples (Table 1) were milled to obtain a particle size distribution of 80% < 74 μm . Coal particles were loaded into a quartz cell and pyrolysed in a furnace at 800°C. A stream of helium delivered the pyrolysis products to the traps for the sampling process. The apparatus is shown in Fig. 1, and was designed to contain up to 0.5 g of coal powder. The connection tubes were also made of quartz for temperature resistance. The cell had an internal volume of 28 cm^3 and, for a faster heating, the sample was deposited only on the bottom of the chamber as a single layer of coal particles. The gas inlet tubing was welded to the cell. Near the top of the inlet tubing, a side opening allowed the introduction of a thermocouple for direct measurement of the coal temperature. The outlet tubing was removable in order to simplify sample loading and chamber cleaning. The opposite end of the tubing was connected to a series of three traps for stepwise collection of the pyrolysis products based on their volatility.

The first trap encountered by the stream of gas was a glass-wool filter (trap 1, 6 $\text{cm} \times 4$ mm), which, because of its lower temperature (55°C), promoted the condensation of the heavy fraction of the pyrolysate. Graphitized carbon black

Table 1
 Characteristics of the coals (as received)^a

Code	Type	Origin	Moisture (%)	VM (%)	FC (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (diff.) (%)	HCV (kcal/kg)
C01	Bituminous	USA, McCall	1.6	27.2	64.9	6.3	80.9	4.9	1	0.9	4.0	7809
C02	Bituminous	USA, I Mapco	3.1	32.7	57.0	7.2	74.4	5.2	1	0.8	8.2	7261
C03	Bituminous	South African I	2.8	24.5	58.9	13.8	72.1	4.4	1	0.5	5.5	6597
C04	Bituminous	Polish I	2.4	29.2	57.2	11.2	74.7	5.0	1	0.7	5.0	7883
C05	Bituminous	Venezuelan I	2.6	35.2	58.3	3.7	79.1	5.9	1	0.5	7.2	6897
C08	Bituminous	Columbian I	5.6	34.0	53.8	6.6	71.1	5.5	1	0.8	10.2	7185
C09	Anthracite	Russian anthracite	4.2	8.7	78.8	8.3	83.7	2.2	0	0.8	0.5	7017
C10	Sub-bituminous	Italian Sulcis	7.5	38.4	37.3	16.8	53.2	5.1	1	6.1	11.9	5071
C17	Graphite	Pinerolo graphite	3.0	5.7	65.1	26.2	66.0	1.2	0	0.9	2.3	5554
C19	Lignite	Spanish lignite	9.4	42.1	27.1	4.1	46.2	5.1	0	11.2	7.7	4717
C25	Bituminous	Russian 5 I	10.2	34.0	48.5	7.3	66.3	5.0	2	0.2	11.2	6405
C43	Anthracite bituminous	Canada, British Columbia 4	0.8	20.8	69.0	9.3	77.2	4.3	1	0.3	7.3	7727

^a VM = Volatile matter; FC = fixed carbon; HCV = high calorific value.

(GCB) was used as the adsorbent material in the other two traps and was used for trapping low-boiling compounds. It usually requires thermal desorption for the release of compounds. GCB is chemically inert and shows several advantages over other adsorbents [20–24]. The compound selection effected by the traps was mainly based on the volatility of the substances, and was achieved by using adsorbents with different specific surface areas. Both traps measured $10\text{ cm} \times 4\text{ mm}$ and the packing material was 40–60 mesh. Carbograph 2 (Carbochimica Romana, Rome, Italy and Alltech, Deerfield, IL, USA), with a specific surface area of $10\text{ m}^2/\text{g}$, was used for the trap 2. Carbograph 1, with a higher specific surface area ($90\text{ m}^2/\text{g}$), was used for trap 3. The addition of a second GCB trap enhanced the adsorption of the more volatile fraction of the pyrolysate not retained by the first trap. A control trap, packed with Carbograph 1, was added at the gas exit to check for the possible breakthrough of compounds.

2.2. Sampling procedure

A 50-mg amount of sample was loaded into the chamber. Larger amounts of sample exceeded the capacity of the traps with a con-

sequent loss of pyrolysate. The furnace temperature was kept constant at 800°C . The cell, filled with the sample and connected with the rest of the apparatus, was equilibrated for 1 min with a 10 ml/min helium flow at room temperature. The gas flow-rate was then kept constant throughout the entire sampling procedure. Once placed in the furnace, the sample reached the final temperature (800°C) after 35 s. The sample was kept inside the oven for a total of 3 min, then cooled and disconnected from the gas line. This time was sufficient to complete the pyrolysis of all samples. The water was trapped in the outlet tubing before the glass-wool trap. A char residue was visible in the quartz cell after each experiment and was not analysed. The product residence time in the hot zone was short enough to prevent the formation of secondary (recombination) pyrolysis products.

2.3. Gas chromatography and mass spectrometry

Two independent GC–MS systems were used for the analysis of the trapped material. The volatile fraction collected in traps 2 and 3 (Fig. 1) was extracted via thermal desorption and injected on-line into a packed GC column coupled to a VG 70/70 H double-focusing magnetic mass

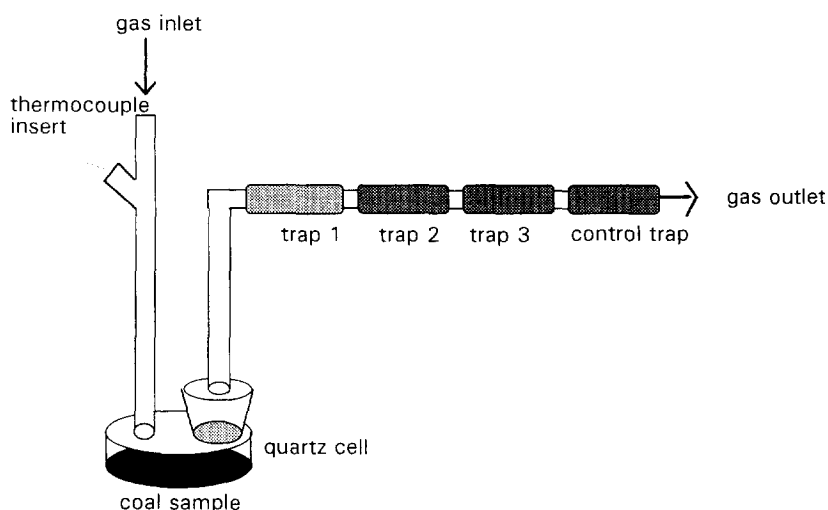


Fig. 1. Sampling apparatus: trap 1, glass-wool; trap 2, Carbograph 2; trap 3, Carbograph 1; control trap, Carbograph 1. Pyrolysate fractions are collected according to their volatility (see text).

spectrometer (Fisons, Manchester, UK). The heavier fraction was extracted from trap 1 with solvent and analysed using a capillary GC column coupled to an HP 5970 quadrupole analyser (Hewlett-Packard, Palo Alto, CA, USA). A 2 m long column was packed with CarboGraph 1 (80–100 mesh), modified with 1% SP 1000, and coupled via a jet separator to the mass spectrometer. These types of columns, because of the higher capacity factor, are particularly suitable for the separation of highly volatile organic compounds.

CarboGraph 2 traps were placed in a laboratory-made oven, kept at 300°C and heated for 60 s before the carrier gas was allowed through and transferred to the column. CarboGraph 1 traps, characterized by a higher specific surface area, were heated for a longer time (120 s).

Helium was used as the carrier gas at a pressure of 1.5 bar. The temperature programme was 40°C held for 4 min, then increased to 200°C at 13°C/min.

A Dani (Monza, Italy) Model 3008 chromatograph was used with the packed column. The mass spectrometer was operated in the total ion current (TIC) mode, scanning from 40 to 250 u with a total scan time (including inter-scan delay) of 1000 ms. Full transmission of the ion beam was implemented with a resulting 10% valley resolution of about 1000:1. Conventional electron impact (EI) ionization was used with electron energy 70 eV, emission current 200 μ A and accelerating potential 4 kV. The ion source and jet separator interface were kept at 200°C. Mass spectrometric acquisition and data processing were performed with a Teknivent (Maryland Heights, MO, USA) Vector-two data system. The scan speed and magnet current ramp were controlled by the original analogue electronic panel.

The condensate fraction from the pyrolysis was extracted from the glass-wool trap and the outlet tubing, and subsequently analysed in the capillary GC–MS system. The glass-wool trap was extracted by percolating 5 ml of methylene chloride through the tube. The procedure was completed by a further extraction step using an ultrasonic bath.

A 30 m \times 250 μ m I.D. Supelco (Bellefonte,

PA, USA) SPB 5 capillary column was employed in an HP 5890 gas chromatograph. The column temperature programme was 40°C held for 1 min, then increased to 300°C at 10°C/min. The samples were injected in the splitless mode at 280°C. The quadrupole mass spectrometer was operated in the TIC mode, scanning from 40 to 350 u in 0.8 s. Selected-ion monitoring (SIM) mode analyses were also performed. The EI ion source was kept at 200°C and the electron energy was set at 70 eV.

Methylene chloride (pesticide grade) was purchased from J.T. Baker (Deventer, Netherlands). Helium of 5.6 purity grade (>99.9996%) was purchased from SOL (Milan, Italy).

3. Results and discussion

The primary aim of this method was to improve the characterization of coals through a deeper investigation of various compound classes commonly found in the pyrolysate, and the sampling and analytical procedures were carried out separately. This method tries to exploit some of the best analytical techniques available for sampling and analysing coal pyrolysate. The sampling and analytical procedures were further subdivided to accommodate better the different chemical properties of the collected compounds with the most suitable analytical technique. This first approach was restricted to GC-amenable compounds. A future study will be devoted to products amenable to LC–MS techniques.

The validity of on-line techniques, such as Curie-point GC–MS, is often compromised by the wide range of different compound classes found in the coal. Hence, a specific on-line method may simultaneously satisfy the conditions for a restricted number of analytes but it will hardly fit the analytical requirements of the rest of products that will be ignored or poorly detected. Our sampling apparatus was developed in order to collect compounds with similar volatility. Suitable GC–MS instrumentation was therefore chosen for the analysis of each group. Volatility is obviously the key chemical property for the correct choice of an appropriate GC–MS

technique. A packed column was used for the highly volatile fractions and a capillary column was employed only for the condensate. Low-boiling products were subdivided in two different traps. The first, packed with Carbo-graph 2, trapped some of the heavier species among this group, such as benzene and toluene. The second trap, characterized by a higher specific surface area, collected the more volatile fraction, mainly composed of C₄–C₆ alkanes unretained by the previous trap. A third trap, packed with Carbo-graph 1, was connected after the second trap. It was used only to check for possible compound breakthrough in the sampling system and it was routinely analysed using GC with flame ionization detection (FID).

All the condensate was collected before the GCB traps and was extracted with methylene chloride. This fraction was very complex and many different compound classes could be found. The extract was analysed by capillary GC–MS to ensure a higher chromatographic resolution and better evaluation of the results.

Medium-rank coals, especially bituminous samples, started to saturate the traps at amounts higher than 100 mg; 50 mg was found to be representative of the original coal samples without showing this drawback. The method repro-

ducibility was evaluated by analysing five samples of the same coal. The standard deviation (9.7%) was calculated by measuring the *n*-C₂₀ peak areas obtained from the analysis of the samples.

Twelve coal samples (Table 1), representative of the entire range of coals rank, were selected for the study. The material trapped in the Carbo-graph 1 and 2 traps was analysed as described under Experimental. The TIC chromatographic peaks were integrated. An amount of 420 ng of benzene was injected before each analysis and used as an external standard. Benzene and toluene contents were determined and their absolute amounts in the 50 mg of sample were reported (Fig. 2).

An approximate calculation was made of the total organic material trapped by the Carbo-graph 1 and 2 traps. The integrated peaks were summed and compared with the area obtained from a standard solution of 5 μg of benzene in the case of Carbo-graph 2 (trap 2) data, and from a standard solution of 5 μg of *n*-pentane for the Carbo-graph 1 (trap 3) data. The results, expressed in micrograms, are reported in Fig. 3. The comparison appears to be very significant. The use of traps with different adsorption properties permitted discrimination among volatile

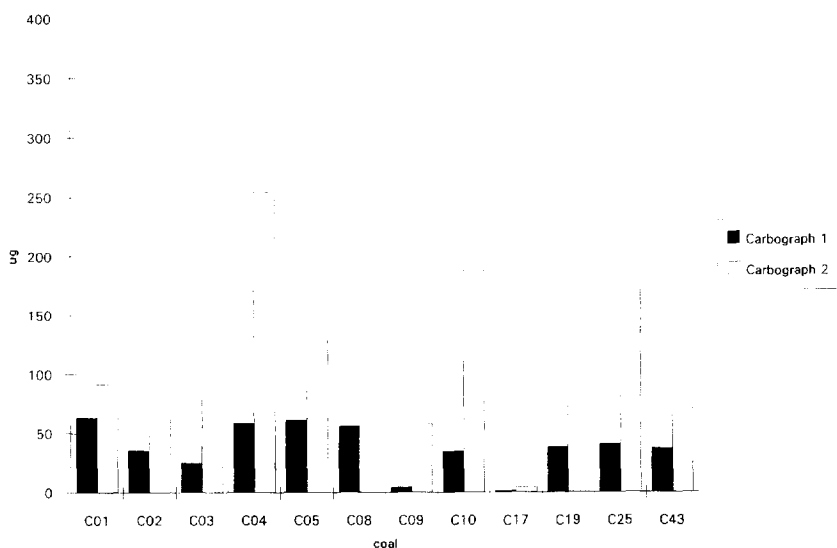


Fig. 2. Amounts of benzene and toluene calculated for 50 mg of sample (trap 2).

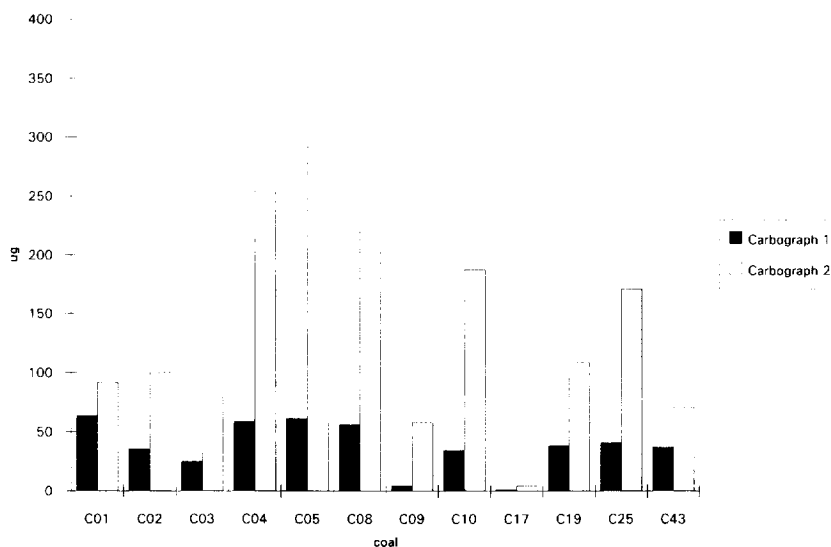


Fig. 3. Total volatile organic material extracted from traps 1 and 2 calculated for 50 mg of sample.

compounds and, further, important characterizations can be outlined. Samples C01, C02 and C03 as C19, C25 and C43 were characterized by a peculiar content of volatile products. In particular, sample C01, a bituminous coal, showed a marked increase of the highly volatile fraction and exceeded that for the other coals examined. Similar considerations apply to other samples. Anthracite and graphite produced the least volatile matter. C04, C05 and C08 were instead rich in organic material in both fractions. These

evaluations were, of course, restricted to a limited amount of sample and cannot be considered representative of the original coals, but they offer a good example of the capabilities of the method.

A capillary column, based on gas-liquid chromatography, was better suited for the analysis of the condensed products. The solution obtained from the extraction of each sample allowed a series of specific GC-MS analyses for the determination of different classes of compounds.

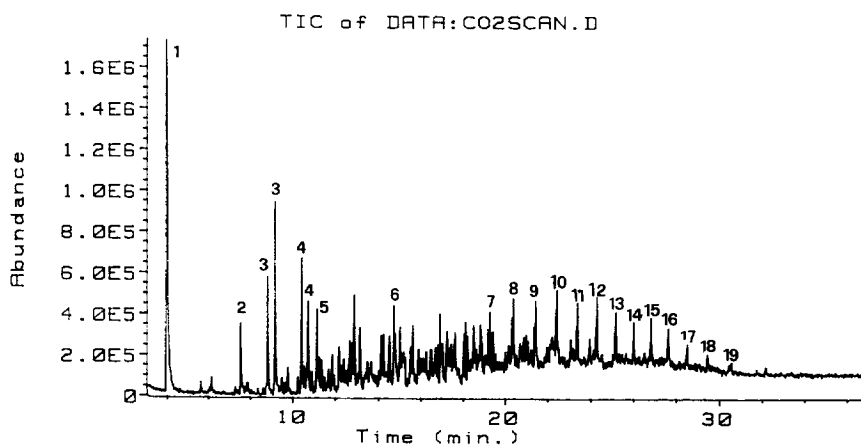


Fig. 4. TIC profile obtained from the condensate of sample C02. Peaks: 1 = toluene; 2 = phenol; 3 = cresols; 4 = dimethylphenols; 5 = naphthalene; 6 = acenaphthylene; 7–19 = C_{18} – C_{30} .

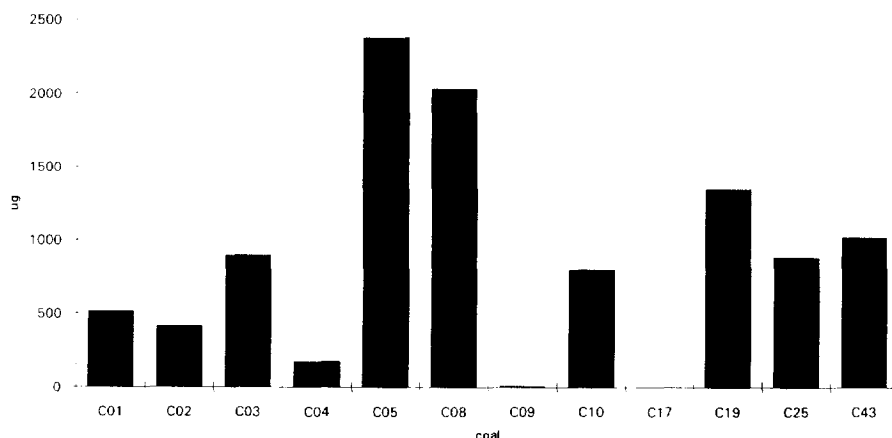


Fig. 5. Condensed organic material extracted from trap 1 calculated for 50 mg of sample.

The extracts were first analysed in the TIC mode in order to evaluate the total organic material present in each sample. Fig. 4 shows the TIC profile obtained from sample C02. The series of *n*-alkane peaks is easily recognizable in the mass chromatogram. Three specific SIM analyses were then performed for the determination of well defined groups of substances: polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes and phenols. A standard injection of 5 μg of *n*-C₂₀ was used to estimate the total amount of organic material collected in each sample. The results were ob-

tained by comparing the external standard peak area with the total integrated area obtained from the TIC profile. These values, expressed in micrograms, are reported in Fig. 5.

It is interesting to outline the broad range of amounts obtained from each coal. C09 and C17, anthracite and graphite, respectively, gave the lowest values and C05 and C08, two bituminous coals, were close to 2.5 mg, almost 5% of the whole sample mass. A similar trend, with some exceptions, is visible in Fig. 6, where the total contribution of *n*-alkanes is reported. For the

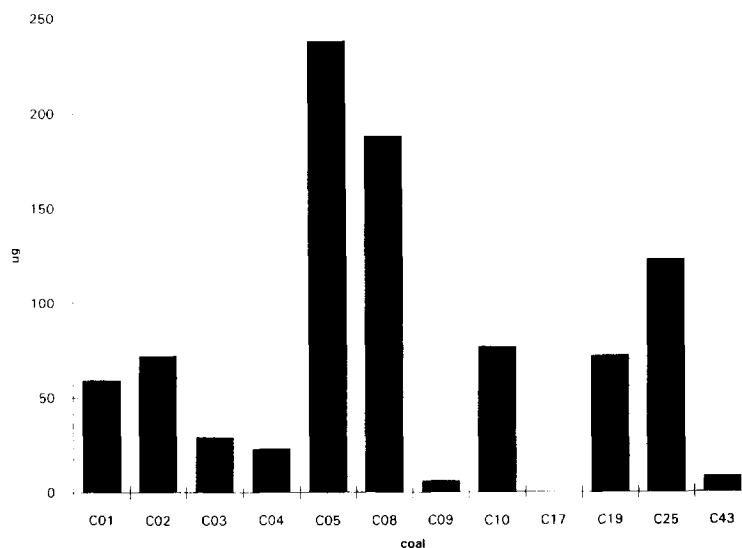


Fig. 6. Contribution of *n*-alkanes in the condensed material (trap 1) expressed in μg for 50 mg of sample.

Table 2
SIM programme for the analysis of PAHs

No.	Compound	m/z	No.	Compound	m/z
1	Naphthalene	128	15	2-Methylanthracene	192
2	2-Methylnaphthalene	142	16	6 Fluoranthene	202
3	1-Methylnaphthalene	142	17	Pyrene	202
4	2,6-Dimethylnaphthalene	156	18	1-Methylpyrene	216
5	1,6- + 1,3-Dimethylnaphthalene	156	19	Brenz[<i>a</i>]anthracene	228
6	1,4- + 1,5-Dimethylnaphthalene	156	20	Crysenes + benz[<i>b</i>]anthracene	228
7	Acenaphthylene	152	21	Benzo[<i>b</i>] + benzo[<i>k</i>]fluoranthene	252
8	1,2-Dimethylnaphthalene	156	22	Benzo[<i>e</i>]pyrene	252
9	1,8-Dimethylnaphthalene	156	23	Benzo[<i>a</i>]pyrene	252
10	Acenaphthene	154	24	Triphenylbenzene	306
11	Fluorene	166	25	Indeno[1,2,3- <i>cd</i>]pyrene	276
12	Dihydroanthracene	180	26	Dibenzo[<i>a,h</i>]anthracene	278
13	Phenanthrene	178	27	Benzo[<i>ghi</i>]perylene	276
14	Anthracene	178			

detection of the alkanes, the mass spectrometer was operating in the SIM mode at m/z 85. Relative concentrations were calculated using a C_{12} – C_{32} external standard. Characteristic trends for the single alkane abundances were also reported; 31 different PAHs were considered in this study (Table 2). A specific SIM programme, based on the characteristic strong molecular ion

signal, was set up for PAH acquisition. The concentrations of the single species were precisely obtained using a solution of 5 μg of the PAH considered. Contributions from unresolved peaks from compounds sharing the same m/z value were added together. The results are summarized in Fig. 7, where the compound number is referred to the list of PAHs reported in Table 2.

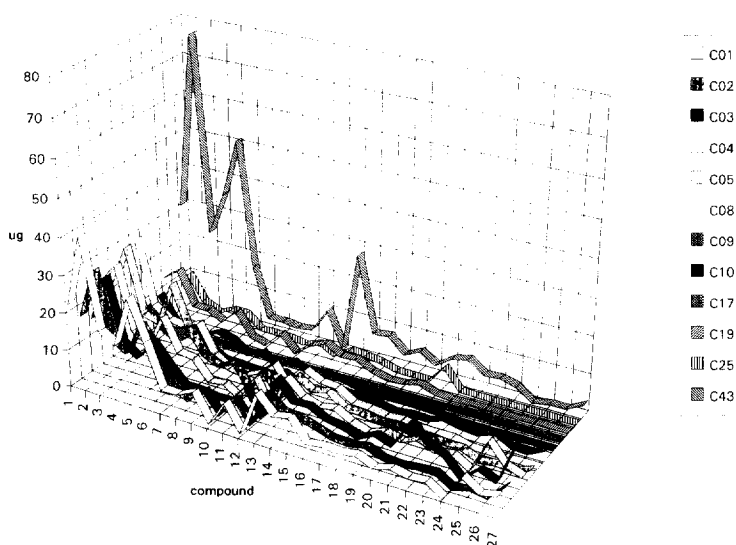


Fig. 7. PAH distribution in the condensed material. Numbered compounds are reported in Table 2. Amounts expressed in μg for 50 mg of sample.

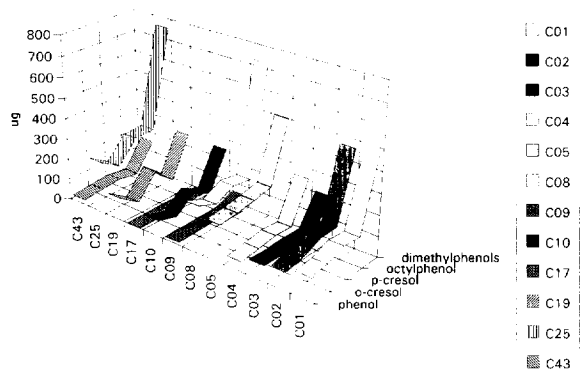


Fig. 8. Phenol distribution in the condensed material. Amounts expressed in μg for 50 mg of sample.

Each sample profile appears well characterized. Sample C43, a bituminous anthracite, was particularly rich in the compounds considered whereas C17, a graphite, gave an undetectable response. The coal samples were also evaluated for the presence of some phenols. MS detection was performed in the SIM mode at m/z 107 characteristic of this group. Again, the evaluation of the concentration of each single phenol was obtained by comparing standard and sample peak areas. The results for the compounds considered are reported in Fig. 8.

In conclusion, the method for the characterization of coals presented in this paper offers an accurate and reliable tool when a deep investigation is needed. This method allows a more functional use of GC and MS in order to suit better the volatility of the compounds under investigation. This gives the possibility of concentrating efforts on a restricted number of compound classes for each step, thus improving the quality of the results.

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