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Programmed-temperature vaporiser injector as a new analytical tool for combined thermal desorption-pyrolysis of solid samples Application to geochemical analysis

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Abstract

This paper describes a new analytical tool for the analysis of geological samples for geochemical purposes. A system is described that allows subsequent thermal treatment at several stages to occur inside the liner of a programmed temperature vaporiser injector (PTV). The samples under investigation are geological hydrocarbon source rock and coal samples. Analysis of the samples is performed in a sequential procedure. A three-step temperature-level procedure is proposed. The system described is inexpensive and easy to operate. The advantage of combining thermal desorption and pyrolysis sequentially inside a PTV injector is the flexibility of temperature selection, as well as the ease of calibration and quantitation. Moreover, the absence of a heated transfer line and heated valves minimises the risk of loss of high-molecular-mass compounds. The method described allows a detailed characterisation of oil and kerogen in a source rock. An atomic emission detector is used to monitor simultaneously the carbon and the sulphur signals for further structural elucidation of the kerogen. The results obtained with this system are in good agreement with those obtained with other pyrolysis systems.

Keywords: Injection methods; Programmed-temperature vaporizer; Geological samples; Oils; Sample preparation; Kerogens

1. Introduction

Thermal sample pretreatment methods, such as thermal de sorption or head-space analysis, are widely used in combination with gas chromatography for sample preparation of liquid or solid samples. A typical application area of thermal sample preparation techniques is the analysis of geological samples for geochemical purposes. Oil-containing rock is analysed using a wide variety of thermal and liquid sample pretreatment techniques to obtain

information crucial to oil exploration and production processes. The most commonly used thermal sample pretreatment methods in geochemical analysis of rocks, are thermal desorption and pyrolysis [1,2]. Thermal desorption is used to study the relatively low-molecular-mass components present in the sample [3,4]. pyrolysis techniques, on the other hand, are used to study the veryhigh-molecular-mass structures (kerogens) present in the rock samples [1,2]. These solutes are not directly amenable to GC. Chemical bonds in the molecules have to be cleaved

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to reveal the information present in these structures. Thermal de- sorption and pyrolysis of oil- and kerogencontaining rocks yield a wealth of information about the composition of the sample, the origin of the kerogens and the oil, on the structures that are eventually degraded to the oil, on the maturity of the source rock and on contamination of the source rock with drilling mud additives. Finally, thermal desorption and pyrolysis of source and reservoir rock also yields information about the amount of oil present.

A well known bulk-method for geochemical analysis is the Rock Eval method [5,6]. Using this method the total amount of hydrocarbons that can be thermally desorbed from a crushed rock sample is measured in a furnace at a relatively low temperature. This thermal desorption step is then followed by a pyrolysis treatment. In the latter step, the kerogen whole rock pyrolysates are quantitated. Various instrumental set-ups have been proposed for the Rock Eval method. In their work, Behar et al. [7], for example, used a microfurnace-based pyrolyzer, whereas Solli and Leplat [8] used a commercially available pyroprobe that was modified for use with capillary gas chromatography (GC) columns.

Another concept has been proposed by Horsfield *et al. [9,10].* In this method, called the microscale sealed vessel pyrolysis method (MSSV), the samples are thermally treated in sealed glass tubes to obtain simulated maturation.

Methods for stepwise thermal desorption-pyrolysis are described by Leventhal [11], Bjoroy *et al.* [12] and Stott and Abbott [13] for examining and characterising hydrocarbons in sedimentary rocks. A liquid nitrogen-cooled cold trap is used to refocus the products during thermal treatment. A detailed description of a multiple cold trap pyrolysis GC system was given by Tang and Stauffer [14,15]. These authors used a pyrolyzer linked to a cold trap unit consisting of ten cryogenic traps arranged radially around a 22-port high temperature rotary valve. Fractions, obtained from treatment at different temperatures, were stored in a trap prior to analysis. With this system, a wealth of information was obtained on activation- and formation energies as well as on the reaction mechanisms associated with oil generation from kerogens and asphaltenes.

The large number of traps and valves, however, makes this set-up expensive and vulnerable. The methods described above allow detailed characterisation of oilcontaining rocks. They suffer, however, from a number of disadvantages. Firstly, the instrumentation used in these methods is expensive, both in purchase as well as in operation costs. Calibration of the systems is difficult. Only the most exclusive models are capable of extended programming for complex, multi-step analyses. Other types are more-or-less one-purpose analysers. Moreover, the systems use heated transfer lines and heated valves, which can act as cold spots. Finally, operation and handling of these systems is relatively complex.

In this paper, an inexpensive and easy-to-operate system for multi-step thermal desorption-pyrolysis with subsequent GC analysis for use in geochemical analysis is described. Thermal treatment of the sample is performed inside a programmed temperature vaporiser (PTV) injector. The PTV is used both as the thermal desorption unit and as the pyrolyzer system. The main goal of this work is to show the possibilities of a PTV injector as an analytical tool in geochemical analysis. The advantages of combining the two techniques sequentially inside a PTV injector are the extremely flexible temperature possibilities and the ease of calibration. Moreover, a PTV injector is standard gas chromatographic instrumentation that is inexpensive in comparison to other pyrolyzer systems. For quantitation, we adopted the approach described by Stott and Abbott [13] where an internal standard is injected directly. As our system basically is a standard GC injector, this approach of quantitation is straightforward.

In the proposed method, the sample is weighed directly into the liner of the injector. This allows relatively high sample intakes, thereby resulting in reduced inhomogeneity problems. With the PTV-based thermal desorption-pyrolysis method, sample amounts ranging from sub-milligram amounts to roughly 2 g can be processed. This makes it applicable for samples differing widely in concentration. Here, however, it must be emphasised that, at large sample loadings, secondary reactions can sometimes occur. The pyrolysis chromatograms obtained are qualitatively compared to those obtained using a resistive-heated pyroprobe (Pt-ribbon) pyrolysis unit.

2. **Experimental**

2.1. *Instrumentation*

The combined thermal desorption-pyrolysis experiments were performed using an OPTIC 600 PTV injector (Ai Cambridge, Cambridge, UK). The PTV injector is shown schematically in Fig. 1. The maximum temperature of the standard injector is 600°C. For this work, the injector was modified by the manufacturer to reach a final temperature of 630°C. These temperatures are high enough for thermal de sorption and pyrolysis to occur, while, at the same time, they enable discrimination-free transfer of the products, up to approximately C_{120}, to the GC-column [16,17]. The liner of the injector has an internal diameter of 3.4 mm, which is large enough to load the sample directly into the liner. To hold the sample in place, the liner contains a Pl-type glass frit in its bottom section. The injector is equipped with a liquid CO_2 cooling system for rapid cooling. The total distance between the sample and the column inlet is less than 10 mm. The system contains no heated transfer lines or valves. Losses of heavy products are therefore minimised.

The GC system used for the multi-step thermal desorption-pyrolysis experiments was a Shimadzu 17A (Shimadzu, Kyoto, Japan) equipped with an advanced flow control
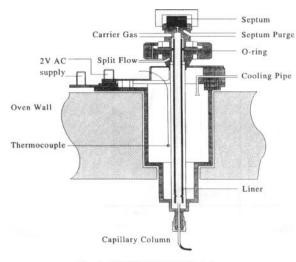

Fig. 1. OPTIC 600 PTV injector.

system. During thermal desorption and pyrolysis, high-molecular-mass fragments are formed [16]. Therefore, the chromatographic system should be capable of programming to a final temperature of at least 425°C. The analytical column used was an HT Simdist CB (10 m x 0.25 mm I.D., film thickness: 0.15 μm) from Chrompack (Middelburg, Netherlands). To avoid leakages, graphite ferrules were used. A flame ionization detector was used. Cryogenic refocussing at the top of the column is necessary, because thermal desorption is a relatively slow process. This was achieved by mounting a laboratory-made cold trap [18] directly below the injector. The trap was made of glass. High temperature graphite ferrules were used for the trap's fittings. The heating wires and the electrical leads were connected with glass-metal connections. To control the cold trap temperature, a temperature sensor was positioned in the centre of the trap, directly adjacent to the column. For more details of the cold trap used see Ref. [19]. The flow control option of the Shimadzu GC was used to keep the column flow constant during the temperature-programmed analysis. A Perkin-Elmer Nelson 1022 system (Perkin-Elmer, Norwalk, CT, USA) was used for data acquisition.

A second series of experiments was performed on another instrument with the same thermal desorption-pyrolysis system. The PTV injector used in these experiments was identical to the one used in the previous experiments. Here, only one temperature level was used. The results obtained with this set-up were used as a comparison with the results obtained on a CDS pyroprobe 100 system (Chemical Data Systems Analytical, Oxford, PA, USA). The experiments were carried out on an HP 5890 series II (Hewlett-Packard, Palo Alto, CA, USA), equipped with an HP-l apolar column (25 m x 0.32 mm I.D., 1.05 μm film thickness). Detection was performed using an HP 5921 atomic emission detector. In these experiments, both the carbon signal and the sulphur signal were monitored. The samples under investigation are of the main kerogen types [20,21]; source rock samples from the Australian region (type I kerogen), the North Sea (type II: marine kerogen) and Malaysia (type III: aromatics and waxes derived from higher landplants). The latter sample was taken at two different depths (5742 ft. and 7330 ft.; 1 ft.= 30.48 cm). All samples were ground before analysis.

2.2. Temperature levels

Thermal desorption at one or more temperature levels followed by pyrolysis gives detailed information about the origin and composition of geological rock samples [3,4,14,15]. To obtain maximum information, a careful selection of the temperature levels used in the combined desorption and pyrolysis treatment is of the utmost importance. If incorrect temperatures are selected, or if insufficient levels are used, important information can be lost. We selected three temperature levels. At the first temperature, the sample should be thermally desorbed under mild conditions (temperatures of about 200 to 300°C). In this step, the sample is analysed for low-molecular-mass components, such as toluene, phenols, xylenes, naphthenes and alkanes up to a carbon number of approximately sixteen, originating from natural processes that occurred over millions of years. These compounds are now desorbed, refocussed in the cold trap, or in the cooled column (see Section 2.3), and analysed. At the next temperature level, components with higher molecular masses are desorbed from the sample $_{(C20-C30)}$. This fraction contains the so-

called "biomarkers", such as isoprenoids, that give important information on the origin of the oil. At this second temperature level, the first signs of degradation of longer alkanes present in the sample start to occur. Doublets of *n*-1-alkenes and *n*-alkanes appear in the chromatograms, indicating that long chain hydrocarbons are broken down. The *n*-1-alkene fraction in these doublets is still low. In the following step, further pyrolysis of high-molecular-mass structures occurs. The ratio between *n*-1-alkenes and *n*alkanes is now almost one. The degradation reactions now occurring are comparable with the natural cracking processes which take place deep under the surface of the earth at high pressures and temperatures [4].

The multistep procedure proposed here consists of three separate chromatographic runs, representing thermal treatment of one sample at 200, 400 and 600°C. At these values, three well-separated fractions of low-molecular-mass components, biomarkers and pyrolysis products were obtained. Some further fine tuning might result in further improved selectivity. This, however, was beyond the scope of the present work. The complete temperature programme of all three sequential GC runs is shown in Fig. 2.

The second series of pyrolysis experiments with atomic emission detection (AED) was carried out at a pyrolysis temperature of 530°C (after desorption at 325°C).
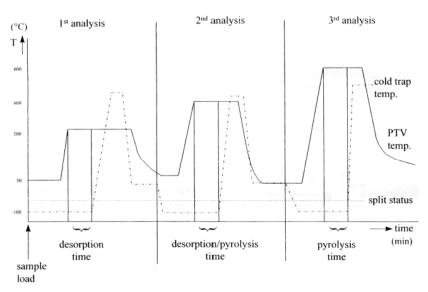

Fig. 2. Total temperature programme of three subsequent runs.

Previous work showed that pyrolysis at 530°C gave the best agreement between pyrograms of source rock and the oil formed from this rock [22]. At this temperature, pyrolysis of the kerogen gives an alkane profile that closely matches that of the oil formed from this kerogen in nature. At this temperature, the results obtained with the PTV set-up can be compared qualitatively with those of other pyrolysers.

2.3. *Methodology*

Prior to analysis, the sample is weighed directly into the liner. The sample amounts ranged from 1 to 10 mg, depending on the organic carbon content of the sample. After inserting the liner into the injector, it was flushed with helium for a few minutes to remove air prior to starting the analysis. Air might lead to deterioration of the GC column and could also induce sidereactions and unwanted degradation products. At the start of an analysis cycle, the injector is cold (50°C) and the cold trap is cooled with liquid nitrogen to -100°C. When this temperature is reached, the injector is heated at a rate of 8°C/s to reach the first temperature level, in this case 200°C. Simultaneously, the GC system and data acquisition are started. The desorption time used is 5 min. After desorption, the cooling of the cold trap is stopped and the trap temperature is rapidly increased to 450°C by applying a current through the heating wires. This is the actual start of the chromatographic analysis. The GC oven temperature programme in all multi-step experiments started at 50°C, with an initial time of 6 min, and ended at 425°C. The programming rate was 10°C/min. The flame ionization detector was maintained at 435°C. The inlet pressure was 65 Kpa, which resulted in a column flow of 2.4 ml/min. The total gas flow through the liner was approximately 135 ml/min, resulting in a split ratio of 1:54. Split injection was applied in order to avoid overloading of the GC column and to reduce the residence times of the products formed during desorption and pyrolysis in the heated zone of the injector. In this way, the formation of secondary pyrolysis products can be minimised [23]. After the first run, the GC, cold trap and injector are cooled down and the second and third step are subsequently executed, all with the same sample.

In the second series of pyrolysis experiments, selective AED was used. The PTV temperature programme started, in this case, at 250°C (after a preceding desorption at 325°C) and increased at 16°C/s to 530°C. The inlet pressure was 100 Kpa and the split ratio was 1:25. The AED operating temperature was 320°C. The GC oven temperature started at an initial value of -20°C (2 min) and was then programmed to 300°C at a rate of 4°C/min and was held there for 10 min. As a thick film column and a low initial oven temperature of -20°C were used in these experiments, no cold trap was needed. The pyrolysis time employed here was 2 min. These experiments were performed to qualitatively compare the results of the PTV pyrolysis with those of "conventional" pyrograms recorded using a resistive-heated pyroprobe pyrolyzer.

3. Results

3.1. *Chromatographic results*

Fig. 3A-C shows the sequential three-step analysis of an Australian source rock sample. The temperature levels applied were 200, 400 and 600°C. As expected, at the first temperature, short-chain alkanes, aromatics and naphthenes are released from the matrix. In the second step, longerchain alkanes (C_{20}-C_{28}) elute from the column. Also, small molecules, such as aromatics, phenols and short-chain alkanes are present in this chromatogram. These products are formed most likely by degradation of very large hydrocarbon structures. At the final temperature of 600°C extensive pyrolysis takes place. Pyrolysis of long chain hydrocarbons results in the typical *n*-l-alkene-*n*-alkane doublets. This is in contrast to the single *n*-alkane homologue-peaks obtained with thermal desorption at lower temperatures. In the pyrolysis step, large amounts of shortchain alkanes such as ethane, propane and butane are formed. The large peak eluting at a retention time of 2 min most probably is methane. Due to its very low boiling point, this component could not be refocussed in the cold trap. Fig. 4A-C shows the analysis of a Malaysian coal sample (type III kerogen) taken at a depth of 5742 ft. Comparison of this sample with a sample taken at the same location but at a depth of 7330 ft. (Fig 5) reveals that
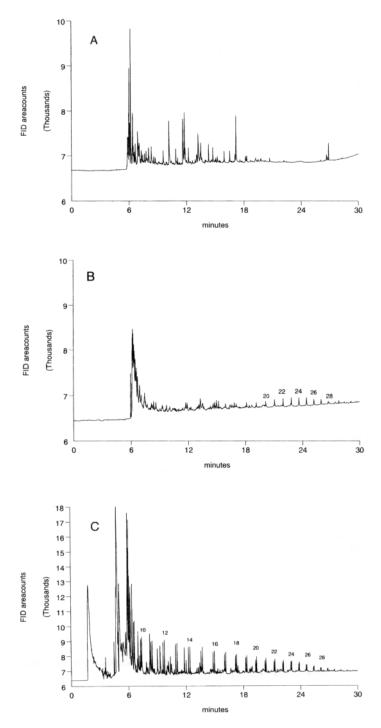
Fig. 3. Three-step analysis of the Australian rock sample. Type I kerogen (aliphatic). Sample intake=9.8 mg. PTV injector temperatures: T-inj .= (A) 200°C; (B) 400°C and (C) 600°C. Numbers are carbon numbers. FID=FIame ionization detection.
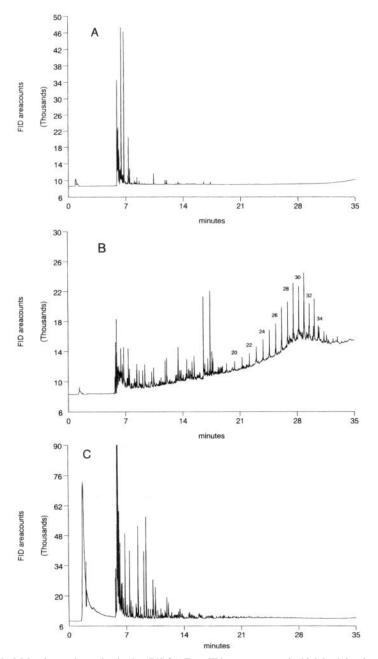
Fig. 4. Three-step analysis of the Malaysian coal sample (depth=5742 ft.). Type III kerogen: aromatic. high landplant input. Sample intake=6 mg. PTV injector temperatures: T-inj.= (A) 200°C; (B) 400°C and (C) 600°C.

thermal desorption at 200°C of the sample taken at 7330 ft. Alkanes up to C24 are observed in this chromatogram. The releases more volatile compounds as well as more higher- large amounts of volatile compounds released and the molecular-mass solutes than the sample taken at 5742 ft. presence of higher-molecular-mass solutes both indicates a
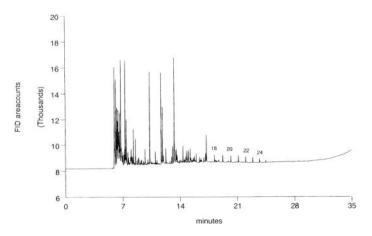
Fig. 5. Malaysian coal sample (depth=7330 ft.). Type III kerogen: aromatic. high landplant input. Sample intake=2 mg. PTV injector temperature (desorption temperature)= 200°C.

higher degree of maturity for the deeper sample [I].

In all GC analyses, a final column temperature of 425°C was used, allowing elution of compounds as high as C_{100} to C_{120}. For the samples studied here, however, no compounds above approximately C_{40} were formed.

In a last series of experiments, the chromatograms obtained using our PTV-pyrolysis system were compared with those obtained using a pyroprobe pyrolyzer. In these experiments, AED was used. In the experiments, both the carbon signal (193 nm) as well as the sulphur signal (181 nm) were monitored. A PTV temperature of 530°C was used in these experiments. Fig. 6A shows the pyrogram (carbon signal) of the Australian source rock sample. This pyrogram shows a typical bimodal distribution, characteristic for a source rock with organic matter derived from both bacterial and higher landplants [21]. Fig. 6B shows the sulphur signal. Fig. 7A,B shows the carbon and sulphur trace of a North Sea source rock sample (type II marine sediment). Fig. 8A,B shows the same signals for a higher landplant derived source rock. In the chromatogram, the more important peaks are identified. A detailed identification of all peaks in the carbon and sulphur chromatograms is beyond the scope of this work. The chromatograms obtained were merely used for comparison with results obtained on a CDS Pyroprobe 100 system. This is shown in Fig. 9. This figure shows a pyrogram of the Australian source rock sample, obtained

with the CDS pyroprobe 100. A comparison of Fig. 6A, showing the Australian source rock pyrogram obtained using the PTV system and the Pyroprobe pyrogram shown in Fig. 9, illustrates the excellent agreement between these two types of instruments. Similar conclusions were also reached for all other samples studied. All pyrograms obtained with the new system were very similar to those obtained with the CDS Pyroprobe 100. The new system proposed here can thus be used as an alternative for other types of pyrolyzers. It also allows thermal desorption experiments to be performed without any instrumental modification. Calibration of the system is easy. A liquid calibration standard can be injected immediately after the thermal desorption-pyrolysis experiment. Calibration is hence straightforward and accurate. Early loss of volatile compounds from the sample during sample loading is prevented as the entire desorptionpyrolysis system can be kept at low temperature during this step of the procedure. Finally, due to its high flexibility, the system can be used in many other GC applications.

4. Conclusions

The new PTV-based thermal desorption and pyrolysi system is a valuable analytical tool for the characterisation of geochemical samples. It is extremely flexible with regard
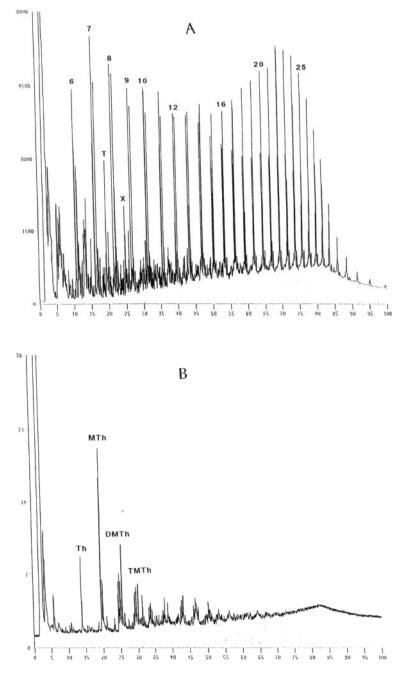
Fig. 6. Pyrolysis at 530°C of the Australian rock sample. Sample intake=7.7 mg; pyrolysis time=2 min, AED detection. (A) Carbon signal (193 nm); (B) sulphur signal (181 nm). Numbers are carbon numbers of l-alkenes/alkanes; T=toluene, X=xylene, Th=thiophene, Mth=methylthiophenes (2,3), DMTh=dimethylthiophenes and TMTh=trimethylthiophenes.
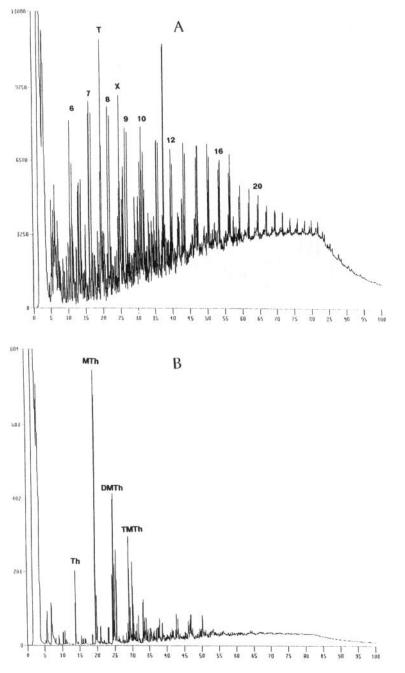
Fig. 7. Pyrolysis at 530°C of the North Sea source rock sample. Type II kerogen: marine sediment. Sample intake=6.0 mg; pyrolysis time=2 min, AED. (A) Carbon signal (193 nm); (B) sulphur signal (181 nm). For peak identification, see Fig. 6.

regard to the temperature levels that can be chosen. The PTV used in this work has a working range from ambient temperature up to 630°C. The system described is easy to

calibrate. Quantitation is straightforward. The relatively high gas flow through the liner keeps secondary reactions

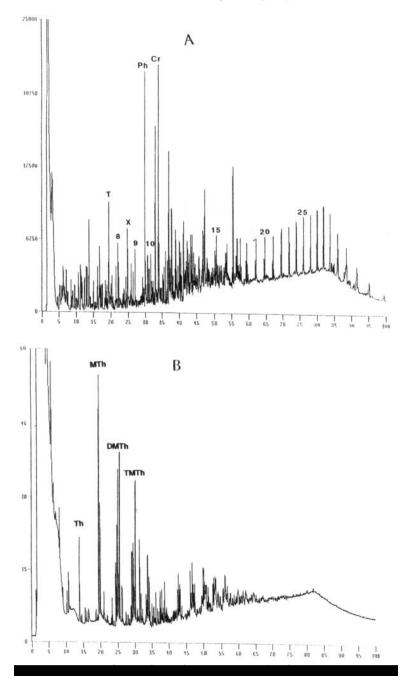*M.P.M. van Lieshout et al. I J. Chromatogr. A 764 (1997) 73-84*

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Fig. 8. Pyrolysis at 530°C of the Malaysian source rock sample. Type III kerogen: aromatic with high landplant input. Sample intake = 1.6 mg; pyrolysis time=2 min, AED. (A) Carbon signal (193 nm); (B) sulphur signal (181 nm). Numbers are carbon numbers of alkanes/alkenes; T=toluene, X=xylene, Ph=phenol and Cr=cresols.
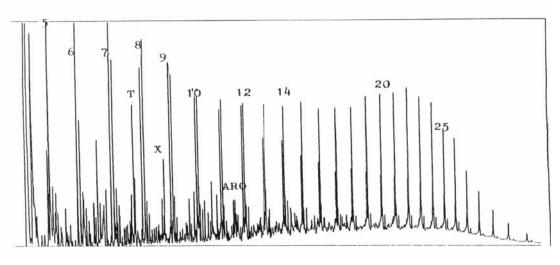
Fig. 9. Pyrogram of Australian source rock (as in Fig. 6A) obtained with a CDS Pyroprobe 100 pyrolyzer. Sample intake=24.9 mg; pyrolysis time=20 s, pyrolysis temperature=530°C, FID. For peak identification, see Fig. 6A.

during pyrolysis to a minimum. Products formed during thermal treatment are rapidly removed from the liner. The pyrograms obtained with the newly developed method agree well with those obtained on a CDS Pyroprobe 100 pyrolysis unit.

The proposed system consists of standard instrumentation, which makes the system cheap compared with conventional thermal desorption and pyrolysis systems. Moreover, it is much more flexible, as it can be used for a number of standard analytical GC injection techniques. The absence of a heated transfer line between the desorptionpyrolysis unit and the GC system, precludes losses of highmolecular-mass components.

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