

Combined Thermal-Desorption and Pyrolysis GC Using a PTV Injector. Part I: Theory and Practice Aspects

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Keywords

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Summary

Thermal sample treatment hyphenated with gas chromatography is a versatile and powerful tool in analytical chemistry. Techniques such as thermal desorption combined with gas chromatography and pyrolysis-GC are widely used for the analysis of samples that can not be introduced directly into the GC. In this contribution a PTV injector is used both as a thermal desorption unit and as a pyrolysis device. In commercially available instruments these two techniques are always separated. An injector with relatively large internal volume was used because this allows weighing the samples directly into the liner of the injector. Only minor adaptations to existing PTV injectors are required. The results obtained with the new method indicate the interesting potentials of the technique as an analytical tool. The absence of a heated transfer line and switching valves, which are generally present in conventional set-ups, eliminates the risk of losses of high molecular weight components. The advantages of combining thermal desorption and pyrolysis sequentially inside a PTV injector include the flexible temperature possibilities and the ease of calibration and quantitation. As an application the system is used for analysis of geological samples for geochemical purposes. The samples under investigation are geological coal samples. The system gives important information about origin, maturity as well as quality and quantity of an oil in a source rock.

1 Introduction

Thermal sample pretreatment methods such as thermal desorption or head-space analysis are widely used in gas chromatography for sample preparation of liquid or solid samples. Thermal desorption is used to study the relatively low molecular weight components present in a sample. Pyrolysis techniques, on the other hand, are used to study the very high molecular weight structures present. These solutes are not directly amenable to GC. Chemical bonds in the molecules have to be cut to have access to the information hidden in these structures. Thermal desorption and pyrolysis yield a wealth of information on the composition of the sample. With thermal desorption low molecular weight compounds can be analyzed after their desorption from the sample matrix, e.g. additives from a polymer sample or light hydrocarbons from a geological sample. While thermal desorption takes place at low and moderate temperature levels, pyrolysis only starts at temperatures above approximately 500°C.

In the present paper a simple, inexpensive and versatile system is described where thermal desorption and pyrolysis subsequently occur in the same instrument. Samples are subjected to a sequence of thermal treatments at different temperature levels inside the liner of a Programmed Temperature Vaporization-injector (PTV). If a PTV injector with a relatively large internal volume is used, weighing the samples directly into the liner of the injector is possible and only minor modifications to the existing injector are required. To retain the sample in the liner, a glass frit has to be installed in the bottom section of the liner. The advantages of using a PTV injector for thermal desorption and pyrolysis are discussed. The applicability of the technique of multistep thermal desorption followed by pyrolysis for the analysis of geological samples is described.

2 Instrumentation

Because high oven temperatures are necessary to elute fragments of high molecular weight formed during desorption and pyrolysis, the chromatographic system used for separation of the products formed should be able to program to a maximum temperature of at least 450°C. The GC used is a Shimadzu 17A (Shimadzu, Kyoto, Japan) which meets this requirement. This GC is equipped with AFC (Advanced Flow Control). The analytical column used was an HT Simdist 10 m x 0.25 mm x 0.15 µm (Chrompack, Middelburg, the Netherlands). This Ultimet-type column is far more rugged than columns drawn from fused-silica. For the on-column experiments a 0.53 mm i.d. metal retention gap (Chrompack) was installed. The PTV injector used was an OPTIC 600 PTV injector. **Figure 1** shows a schematic drawing of this PTV injector.

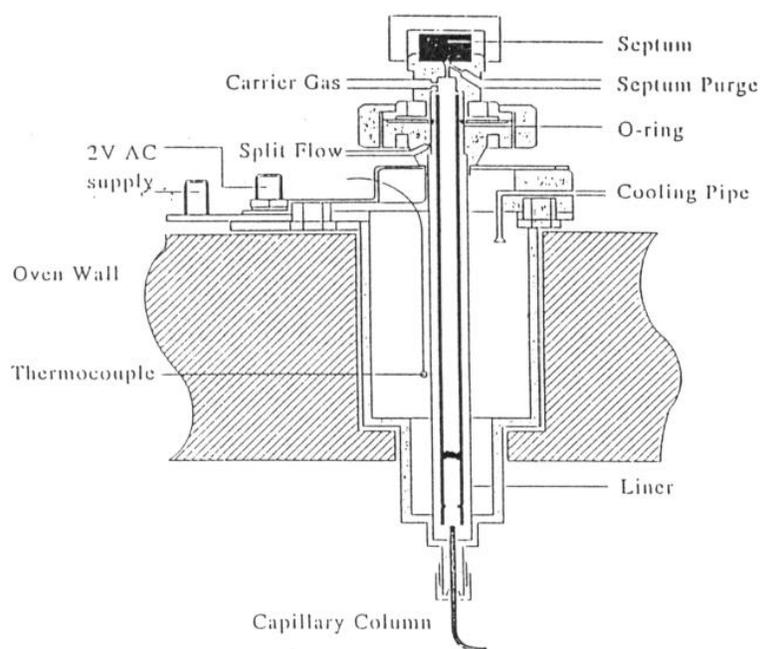


Figure 1

Figure 1. The Optic 600 PTV injector.

The maximum temperature of this injector is 600°C. This is high enough for pyrolysis of a variety of samples and subsequent discrimination-free transfer of the products to the GC-column [1-3]. The liner of the injector has an internal diameter of 3.4 mm. The samples were loaded directly into the liner. To hold the sample in place, the liner contains a glass frit in its bottom section. These glass frit liners were made in house. Care was taken to keep the pressure drop over the

glass frit as low as possible. Moreover, the frit should be as thin as possible to keep activity to a minimum. The detector used was an FID. Because thermal desorption is a relatively slow process, cryogenic refocusing of the products formed at the entrance of the column is necessary. This was achieved by mounting a home-made cold trap [4] directly below the injector. A detailed representation of this cryotrap is shown in **Figure 2**. The trap is made of glass. The heating wire and the electrical leads are connected with glass-metal connections. The cooling agent is liquid nitrogen. The temperature sensor used to control the trap temperature is positioned in the centre of the trap, close to the column. The glass wall of the trap keeps heat transfer from the cryotrap to the oven or from trap to injector to a minimum. The thermo-couple used is a 0.2 mm K-couple with a temperature range from -200°C to 500°C. For data acquisition a Perkin Elmer Nelson 1022 system is used (Perkin Elmer, Norwalk, CT, USA).

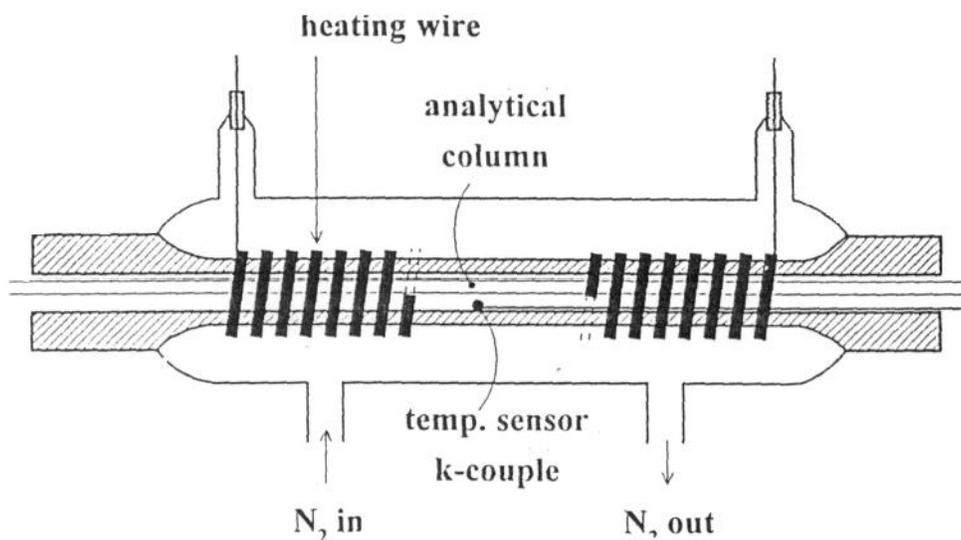


Figure 2. Schematic representation of the home-made cold trap.

3 Geochemical application

The thermal desorption/pyrolysis system described above is used for the analysis of geological samples for geochemical purposes. The samples under investigation are two Malaysian coal samples, taken from different depths. The samples are subjected to thermal treatments at several temperatures. One sample is subsequently treated at increasing temperature levels.

3.1 Temperature levels

Thermal desorption at one or more temperatures followed by pyrolysis can give a wealth of information on the composition of all kinds of samples. For geological samples it gives detailed information about the origin, maturity and composition of the rock samples. For maximum performance careful selection of the temperature-levels for desorption and pyrolysis is of utmost importance. If incorrect temperatures are selected, or if insufficient levels are used, significant information can be lost. The lowest temperature should be selected in a way that low molecular weight compounds can desorb from the matrix and can be determined. Low molecular weight components present in the sample, originating from natural processes that occurred during millions of years, are now desorbed, refocused in the cold trap and analyzed. At the next intermediate injector temperature, moderate molecular weight components are desorbed from the sample. These so called "biomarkers" give important information on the origin of the oil. Also the

first signs of degradation of longer alkanes start to occur. In the following step or steps the remaining very high molecular weight hydrocarbons pyrolyse. The degradation reactions now occurring are comparable with the natural cracking processes which take place deep under the surface of the earth at high temperatures and pressures. The multistep procedure proposed here consists of three separate chromatographic runs, representing thermal treatment of one sample at three different temperatures. The temperature levels selected are 200, 400 and 600°C. The complete temperature program of all three sequential GC-runs is shown in **Figure 3**.

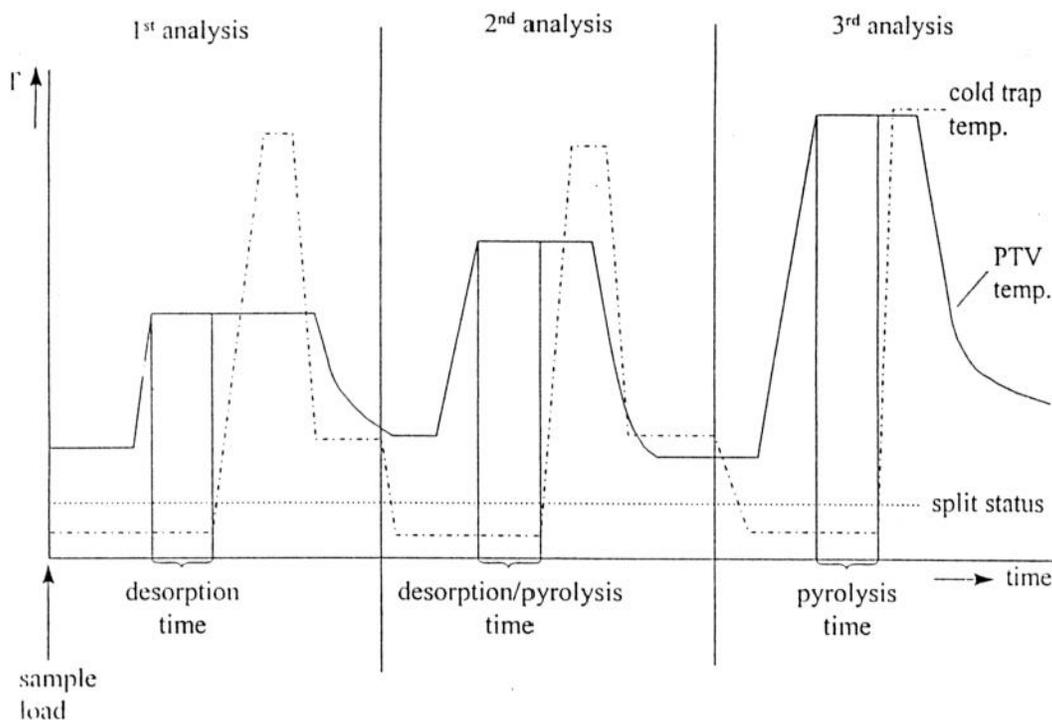


Figure 3. Total temperature program of three sequential runs.

3.2 Chromatographic conditions

The GC temperature program in all experiments started at 50°C (6 minutes) and ended at 425°C. The programming rate was 10°C/minute. The Fill was maintained at a temperature of 435°C. The inlet pressure was 65 kPa, which resulted in a column flow of 2.4 ml/min. A split ratio of 1:54 was used. The linear gas velocity inside the column was 58 cm/sec. The Advanced Flow Control option of the GC was used to keep the column flow constant during the temperature programmed analysis.

4 Chromatographic results

Figures 4 a, b and c show the analysis of the Malaysian coal sample taken at a depth of 5742 ft. The first thermal desorption step shows a high amount of lower alkanes and aromatics. If this step is compared with the same thermal treatment of a sample taken at 7330 ft. (**Figure 5**), it is seen that the thermal desorption at 200°C of the deeper sample gives much more volatile compounds than the sample taken at 5742 ft. This indicates a higher degree of maturity for the deeper sample.

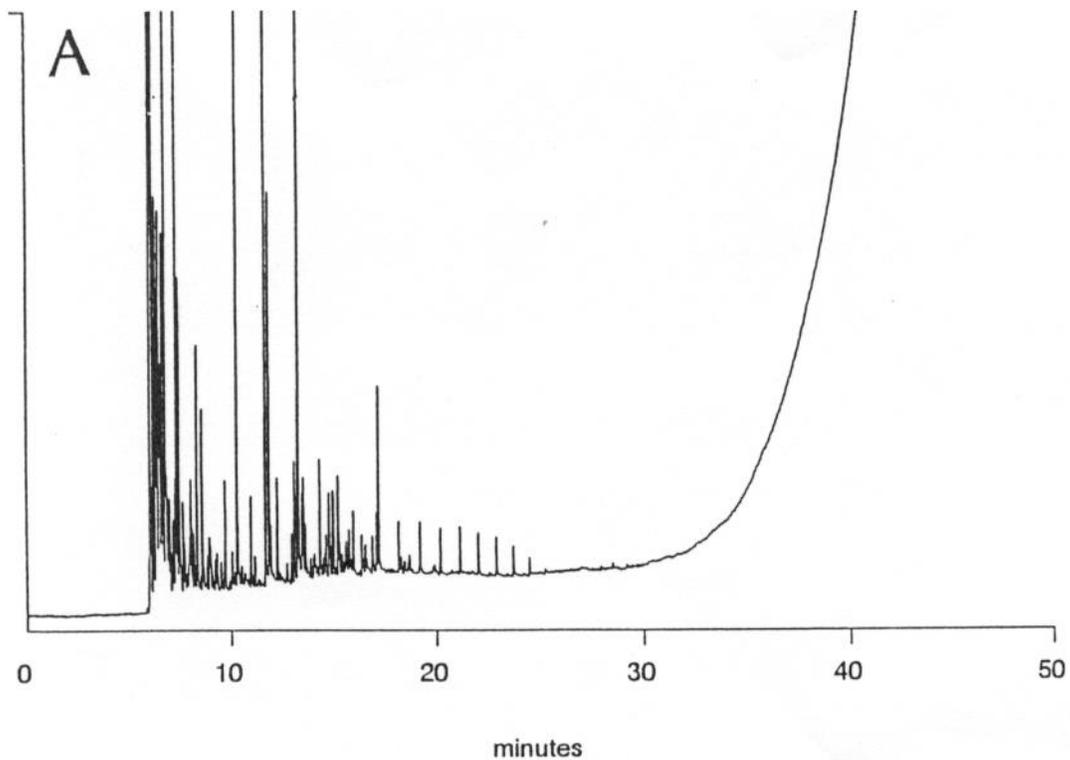


Figure 4a. Malaysian coal sample (5742 ft.) treated at 200°C.

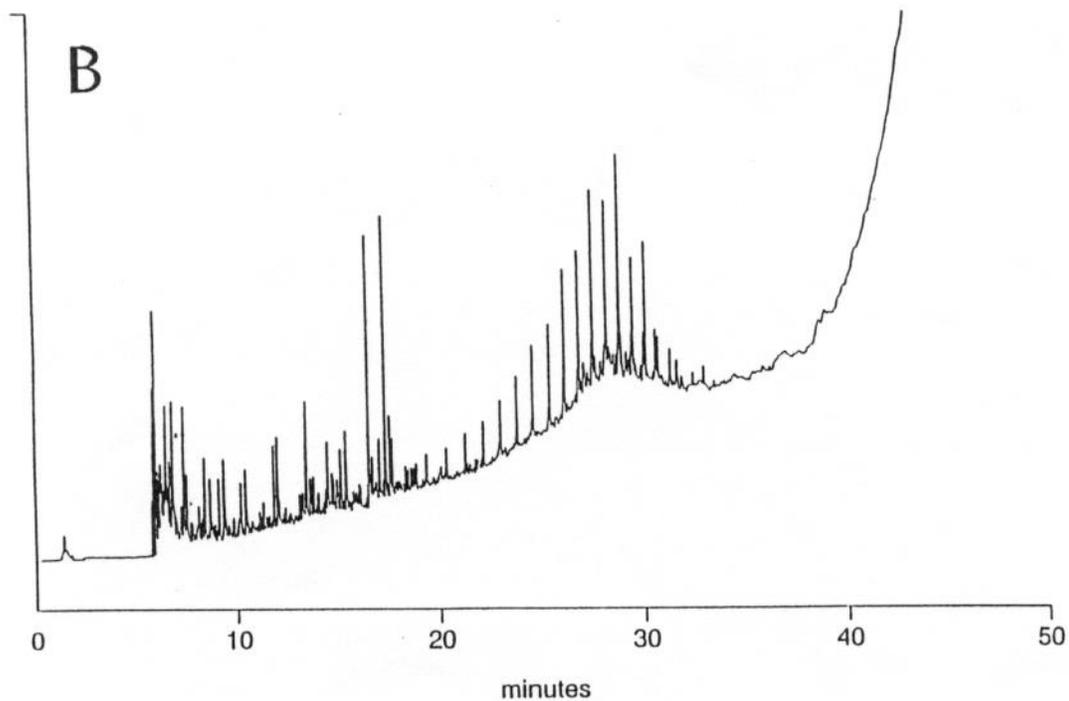


Figure 4b. Malaysian coal sample (5742 ft.) treated at 400°C.

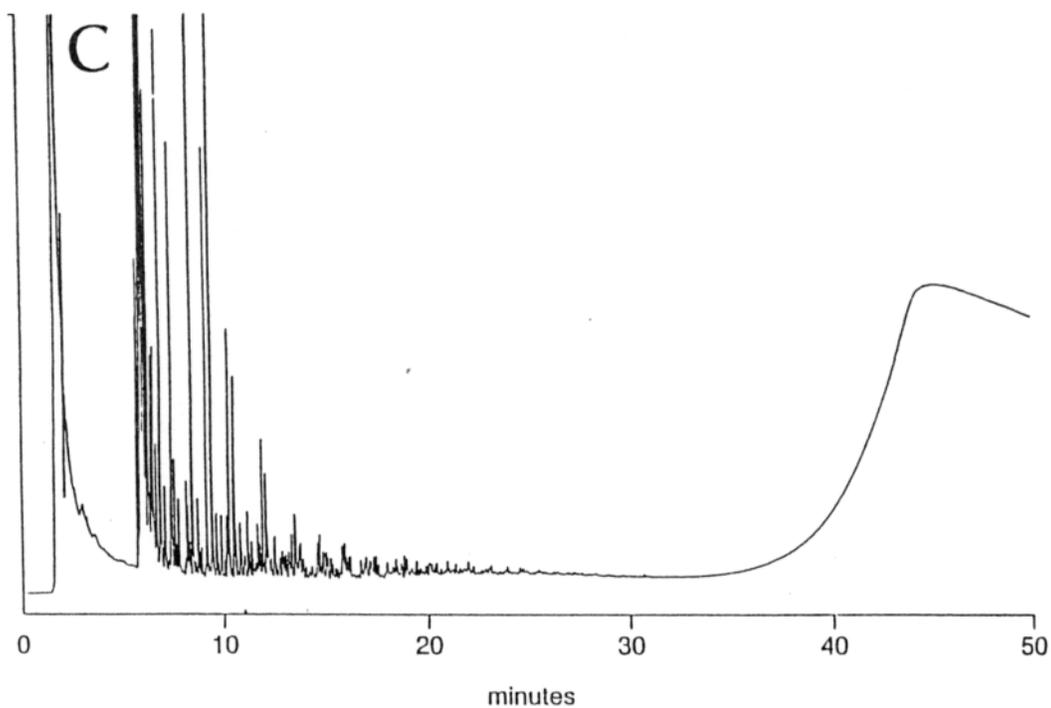


Figure 4c. Malaysian coal sample (5742 ft.) treated at 600°C.

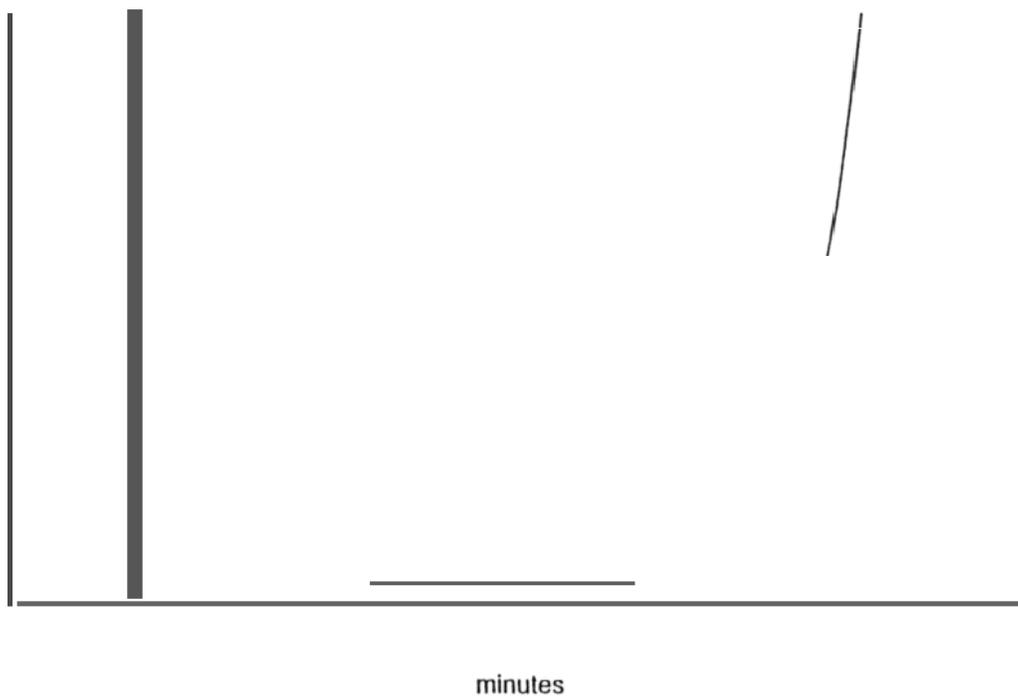


Figure 5. Malaysian coal sample (7330 ft.) treated at 200°C

5 Conclusions

The new PTV-based combined thermal desorption and pyrolysis system has interesting potentials and is a valuable analytical tool for characterization of solid samples such as geochemical rock samples. It is extremely flexible with regard to the temperature levels that can be chose. Sequential thermal desorption and pyrolysis of geological samples gives a tremendous amount of information about origin, maturity, quality and quantity of an oil source rock. The system described is easy to calibrate and consists of standard instrumentation which makes it cheap as compared to conventional thermal desorption and pyrolysis systems. Because a heated transfer line between the desorption-/pyrolysis unit and the GC is absent, the risk of loosing high molecular weight components is kept to a minimum.

References

1. H.P.M. van Lieshout, H-G Janssen, C.A. Cramers in "Proceeding of the 16th International Symposium on Capillary Chromatography", P. Sandra and G. Devos (eds.), Riva del Garda, Italy, Huethig Verlag, Heidelberg, (1994) 1112.
2. G. Schomberg in "Sample Introduction in Capillary Gas Chromatography", Vol. 1, P. Sandra (ed.), Huethig Verlag, Heidelberg, (1985), chapter 4.
3. F. Poy, L. Cobelli in "Sample Introduction in Capillary Gas Chromatography", Vol 1, P. Sandra (ed.), Huethig Verlag, Heidelberg, (1985), chapter 5.
4. T.H.M. Noij, "Trace Analysis by Capillary Gas chromatography, Theory and Methods", Thesis Eindhoven University of Technology (1988).