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CONTINUOUS THERMAL VOLATILIZATION ANALYSIS OF POLYMERS BY GAS CHROMATOGRAPHY WITH PSEUDO-RANDOM INJECTION OF SAMPLES

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SUMMARY

Cross-correlation chromatography was applied to the continuous thermal volatilization analysis of polymers. The *in situ* sampling system with pseudo-random injection of samples is useful for analysing the mechanism of decomposition reactions.

INTRODUCTION

While literature reports on on-column flash pyrolysis have been extensive in the past decade[1-4], there have been few data on the on-line gas chromatographic (GC) analysis of gases evolved from non-volatile materials at low temperatures (up to 500°). The latter analysis is concerned with organic volatiles evolved from a bulk of non-volatile materials at temperatures of practical importance. For example, it is often of interest to establish the gases that are evolved from a fibre at the working temperature and whether any hazardous material is evolved from the fibre during its processing.

Shen[5] reported an *in situ* sampling system for the analysis of gases evolved from non-volatile materials. Using the *in situ* sampling system, the gases can be prepared directly in a GC injection port and transferred *in situ* into a GC column without using a syringe. Yamada *et al.*[6] described a coupled simultaneous technique which gives a differential thermal analysis (DTA)–GC combination. The evolved volatiles are trapped at short intervals in a corresponding number of GC columns kept at low temperatures and then the columns are connected successively to the injection port of the gas chromatograph in order to analyze the volatiles. Different trapping of the degradation products according to their volatiles has been carried out by McNeill[7].

These examples illustrate that the techniques used are completely manual, time consuming and difficult to perform. Indeed, it is easy to inject the *in situ* prepared gases into a chromatographic column using a multi-port switching valve, but the next analysis is possible only when the preceding analysis is completed, when all interesting events may also be completed. The trapping is possible at short time intervals, but it requires the use of an unrealistic number of traps and several undesirable effects may occur.

Nowadays, using minicomputers it is possible to set up new types of experiments. In chromatography, one of these experiments is cross-correlation chromatography (CCC)[8]. This technique can be used in the thermal volatilization analysis of non-volatile materials by GC. In CCC, a sample is introduced sequentially into a chromatograph following the pattern of a pseudo-random binary sequence (PRBS). The time interval between the injections is about 1 sec and chromatograms of interest could be recovered every second. The analysis is completely automatic. The aim of this paper is to demonstrate the use of CCC for continuous monitoring of the kinetics of the thermal degradation of polymers.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The *in situ* sampling system consists of the injection port of the chromatograph (heating chamber) where a solid sample can be heated to 500° and a valve system for transferring the evolved gases from the heating chamber into the GC column. The valve system consists of a Pye pneumatic chromatography valve operated by two solenoid valves.
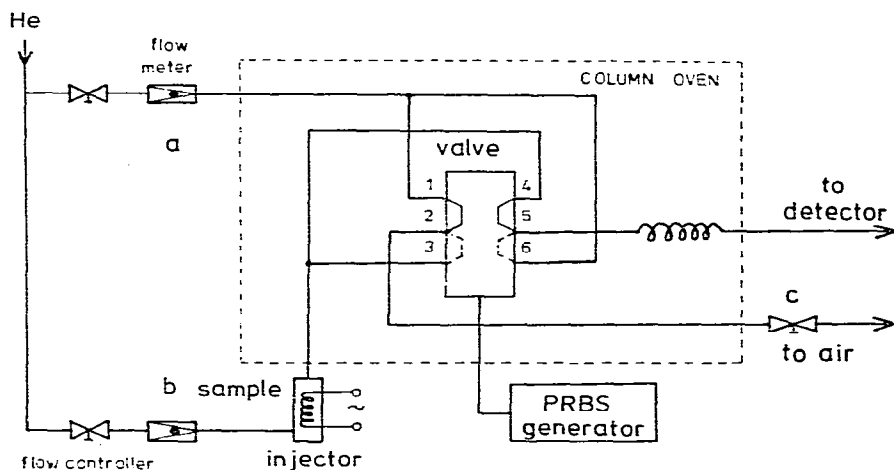

Fig. 1. Experimental arrangement. The broken line indicates the oven of the chromatograph. If PRBS is "on" then 1, 2 and 4, 5 are connected, otherwise 2, 3 and 5, 6 are connected.

The home-made pseudo-random binary sequence generator monitors the on–off state of the solenoids. In all experiments the pseudo-random binary sequence has 63 elements (N) and between two pulses of the generator there was a time interval (Δt) of 4 sec. Thus the lengths of the chromatograms were $N\Delta t = 252$ sec. The chromatographic column was packed with Apiezon L on Inerton AW. The oven temperature was 90°.

Analogue signals from the flame-ionization detector were transformed to digital signals via an analogue to digital converter, and a Videoton 1010 B computer (Hungary) was employed. A multi-channel analyser with a plotter was used to plot the results of the computation. The fast Hadamard transform with necessary per-

mutations was used to convert the output signal into the desired set of chromato-grams[9]. All of the computer programs were written in Fortran.

The valve system must be carefully designed in order to avoid baseline insta-bilities and "ghost" peaks. The resistances of the flow controllers A and B must be equal and the resistance of the flow controller C must be identical with the resistance of the column, otherwise peaks resulting from pressure changes appear on the chromatogram.

RESULTS

Some fibres were pyrolysed by increasing the temperature linearly from 200° to 500° at the rate of 5°/min. The evolved gases were analysed in the system described in order to demonstrate the performance and capabilities of CCC. The fibres used were poly(vinyl alcohol) (Vinol), viscose (Viskos), poly(vinyl chloride) (Klorin) and polyamide (Kapron). The results are presented in Figs. 2–5.
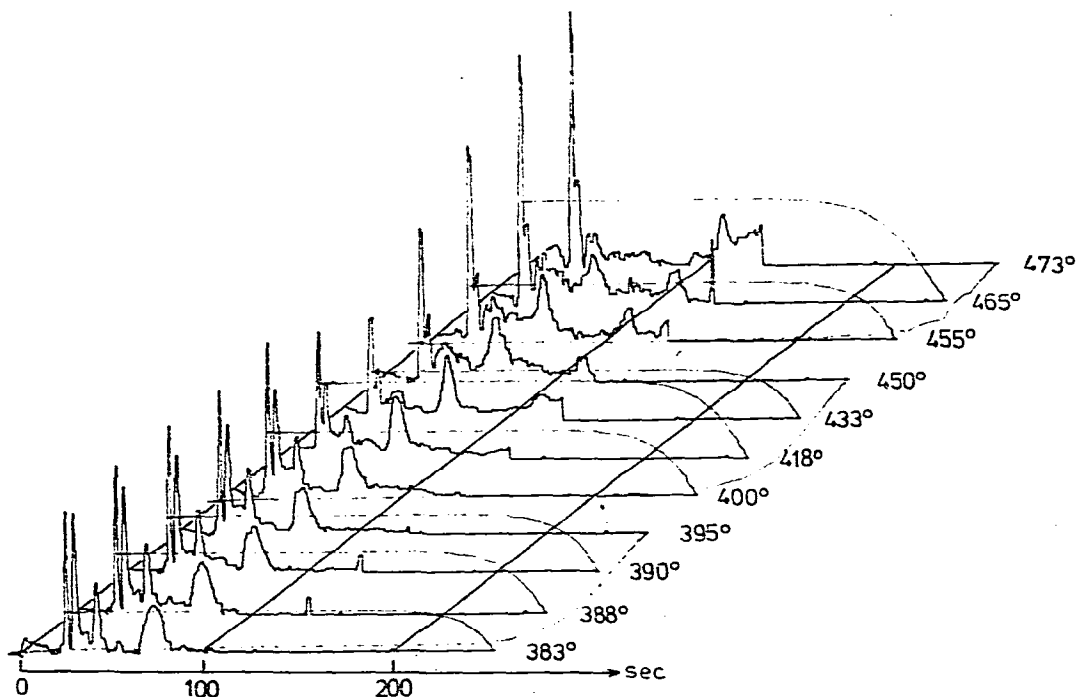

Fig. 2. Chromatograms of the gases evolved during the heating of the poly(vinyl alcohol) fibre.

It is evident from Figs. 2–5 that several changes in the degradation kinetics take place during the heating of the polymers, and it is necessary to follow the appearance of new peaks in the chromatograms in addition to changes in the intensities of particular peaks.

The peaks require identification in order to be able to interpret the results, but that was not the aim of the present work.
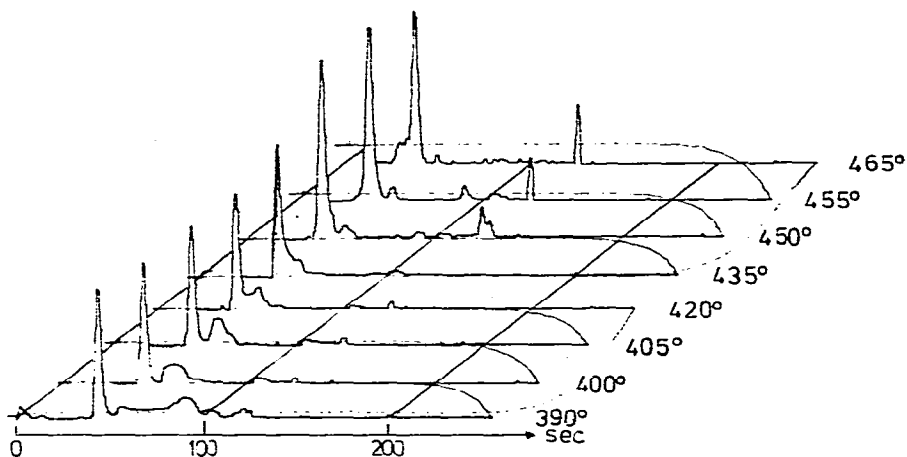
Fig. 3. Chromatograms of the gases evolved during the heating of the poly(vinyl chlorid) fibre.
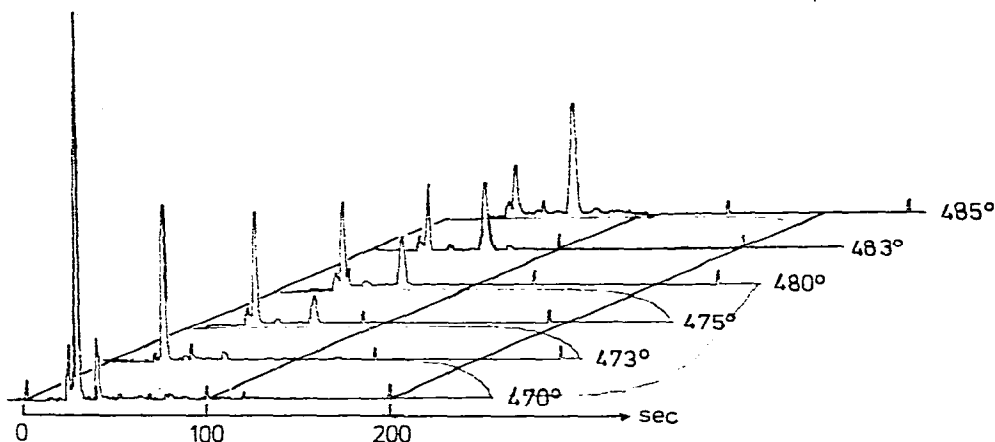

Fig. 4. Chromatograms of the gases evolved during the heating of the viscose fibre.

DISCUSSION

We have found that the use of the *in situ* sampling system with pseudo-random injection of samples facilitates the thermal volatilization analysis of non-volatile materials. It simplifieds the sampling procedures and makes them automatic so that one can easily set up a similar system in a polymer processing laboratory to monitor the gases evolved from various polymers. It can be concluded that this system is useful for analysing the mechanism of decomposition reactions and also permits the kinetic analysis of several reactions that may take place. This kind of information is difficult to obtain from high-temperature (500–900°) pyrolysis results.

CCC is easy to couple with DTA or thermogravimetry (TG). As has been shown by the analysis of various fibres, recording can be performed in very narrow temperature ranges during the thermal degradation and also at many temperatures, so that the peak area of each component of the evolved gases could readily and precisely be plotted as a function of temperature.
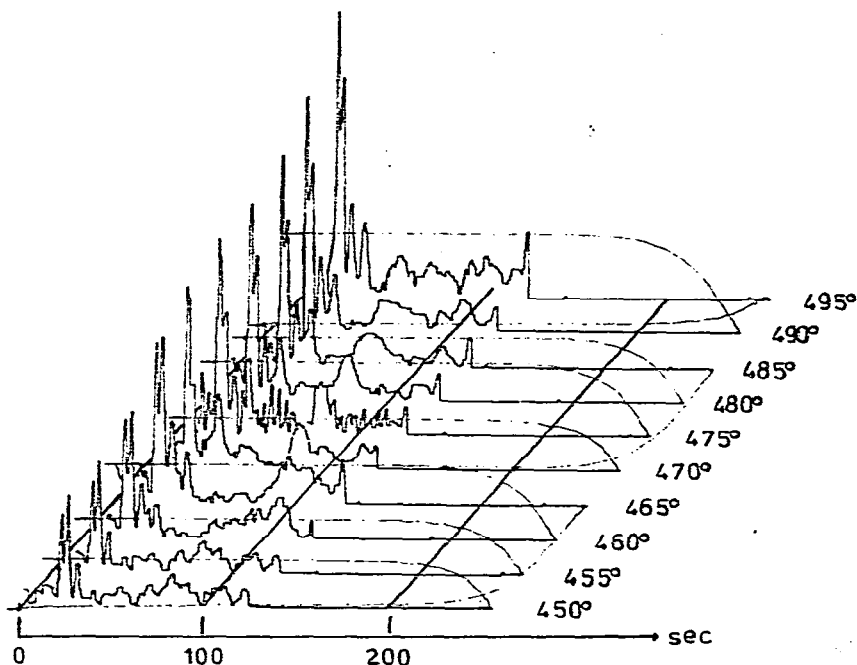
Fig. 5. Chromatograms of the gases evolved during the heating of the polyamide fibre.

Hence the system described gives data that are easy to compare with TG data. For this purpose, a chromatogram at a particular temperature must be integrated to give a point on a TG derivative curve.

However, the problem of the identification of the peaks remains and any on-line GC–spectroscopic technique cannot help in CCC because there is no physical separation of the components in CCC. This, of course, could be achieved by other techniques[3].

ACKNOWLEDGEMENTS

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