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ANALYSIS OF VOLATILES IN POLYMERS BY GAS CHROMATOGRAPHY

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SUMMARY

A survey is made of sampling systems used in gas chromatography. The application of a sampling device for gas chromatographic analysis of volatiles in polymers based on the principle of breaking off the tips of glass ampoules is described. The possibilities are discussed of the multipurpose application of this device as a sampling device for heterogeneous systems and as a microreactor for various chemical reactions with subsequent analysis of the volatile products.

Examples are given of the application of the device in the study of polyethylene cross-linking, in analyzing the decomposition products of peroxides, for the determination of volatiles in butadiene-styrene paper-based laminates, for following polyester-imide varnish curing and for the identification of polymers by the analysis of low-molecular-weight pyrolysis products.

INTRODUCTION

Synthetic polymers always contain small amounts of the parent monomers and residues of auxiliary materials. In addition, a number of low-molecular-weight compounds such as antioxidants, plasticizers, solvents and cross-linking agents are added to polymers to give the polymers desirable properties.

In the case of volatile constituents that can be transferred into the gaseous phase under the conditions of gas chromatography (GC), the advantages of the GC separation method may be fully utilized in their analysis. The choice of a suitable sampling technique, however, presents a problem.

In the analysis of insoluble, viscous or solid substances containing low-volatile or thermally unstable non-volatile constituents, the common sampling techniques can be applied only with certain modifications or must be replaced by a different method. Recently, a number of special sampling methods have been suggested, which can be divided into the following categories:

(1) Modified injection blocks, in which the injection inlets are modified in such a way that the evaporation zone of the gas chromatograph is not contaminated by non-volatile compounds. In the modification a section of the inlet to the evaporation zone can generally be removed¹⁻⁷. However, the applicability of this system is limited.

(2) Injection sampling of solid substances. This modification of sampling systems involves modification of the syringe, mainly of its needle⁸⁻¹⁷. This method does not require modification of the gas chromatograph inlet but it is limited to pulverized and higher-boiling materials without light volatile components.

(3) Moving sampling vessels and capillaries in two-chamber systems. Most systems in this category are based on the principle of traversing the sampling vessel or capillary with the sample under the influence of its own weight, by means of a magnet or a rod, into the heated space of the evaporator. Several variations of this method are known¹⁸⁻²⁸. The system is widely applicable and solves most of the above difficulties except the analysis of substances with highly volatile components.

(4) Encapsulation technique. The samples are sealed or packed into glass, metal, gelatine or other ampoules which are then inserted into the evaporator with a two-chamber system. Here the ampoules are either crushed or melted and so allow the volatile portions to evaporate²⁹⁻³⁸. All materials under consideration may be analyzed in this way. Residues, contaminating the evaporator after crushing or melting of the ampoules, must be periodically removed.

(5) Other systems. There are many other systems which cannot be classified into the above groups³⁹⁻⁴⁸. None of them is widely applicable or fulfils all the basic requirements mentioned above.

On the basis of this knowledge we decided to use the encapsulation technique and to modify it so that the ampoules are not completely crushed; only the two tips are broken off so that the volatile constituents are flushed into the chromatographic column by the carrier gas and the non-volatiles remain in the ampoule. Under such conditions, the ampoule not only gives a means of dosing samples of different phases and consistency but also acts as a microreactor in which various chemical reactions can be carried out before analysis, such as pyrolysis, to study the processes that produce volatile compounds.

EXPERIMENTAL

We have developed a sampling device⁴⁹ as shown in Fig. 1. It consists of an axially drilled cylindrical block of stainless steel (1) with an evaporator chamber of I.D. 5.5 mm and an inlet (2) and outlet (3) for carrier gas. Threads cut at both ends allow the gas-tight sealing of fixed (4) and moveable (5) plungers by means of a Teflon seal (6), stainless-steel rings (7) and nuts (8). The upper part (9) is used to move the moveable plunger downwards with the aid of a spring (10), being operated by a trigger (11). The evaporator chamber is wrapped with resistance wire (12) and with several layers of glass tape (13) as thermal insulation, allowing heating up to 250°. The device is fixed to the gas chromatograph (Carlo Erba, PAID/f type) with the aid of a metal frame.

The sampling ampoules (14) are made of 5 mm O.D. glass tubing in such a way that the ends are drawn into conical tips of about 10 mm in length. In the analysis of solid or viscous substances, however, a glass- or quartz-wool plug is inserted into the ampoule through the open end, followed by the sample, and finally the ampoule is sealed in the above manner. In the sampling of liquids, after inserting the wool the end of the ampoule is drawn out into a narrow capillary through which the required amount of sample is injected with a syringe and the end of the capillary is sealed.

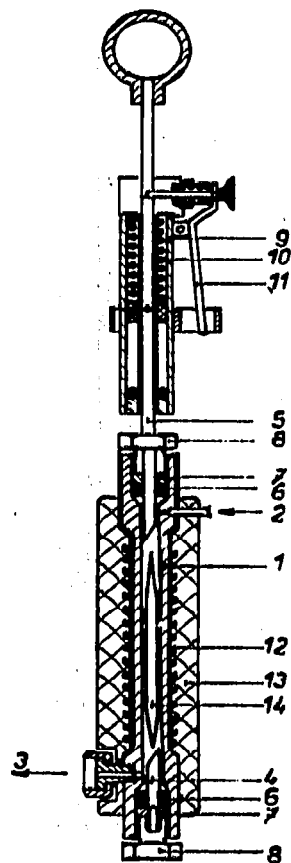


Fig. 1. Sampling device with breaker of ampoule tips. 1 = Stainless steel cylinder of I.D. 5.5 mm; 2 = inlet and 3 = outlet for carrier gas; 4 = fixed plunger; 5 = moveable plunger; 6 = Teflon seal; 7 = stainless-steel ring; 8 = nut; 9 = shifting mechanism; 10 = spring; 11 = trigger; 12 = resistance wire; 13 = thermal insulation; 14 = glass ampoule.

In this way, even highly volatile liquids, such as acetone or ether, may be sampled reproducibly. If a defined atmosphere in the ampoule is required, the drawn capillary of the ampoule is connected to a three-way stopcock with a rubber tube. One arm of the valve is attached to a vacuum pump and the other to a reservoir of the required gas. Air is expelled from the ampoule by alternating evacuation and gas supply, and finally the ampoule is evacuated or the required gas is substituted for air.

Before an analysis is carried out, both necks of the sealed ampoule tips are notched with a file, the moveable plunger is wound up, the ampoule is pushed into the sampling block by means of a fixed plunger and after fastening with a nut the block is flushed with carrier gas for a short time. Then the trigger is actuated, the ampoule tips are broken off by a stroke of the upper plunger and the carrier gas flushes the volatile products into the chromatographic column.

PRACTICAL APPLICATIONS

Polyethylene cross-linking, polyester-imide varnish curing, the analysis of volatiles in butadiene-styrene laminates and polymer identification by pyrolysis were studied as examples of the application of the above sampling technique.

Polyethylene is used for the insulation of high-frequency cables after cross-

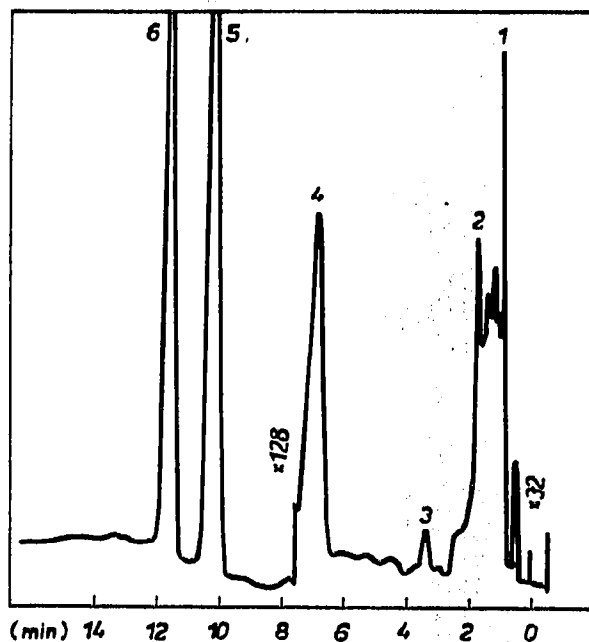
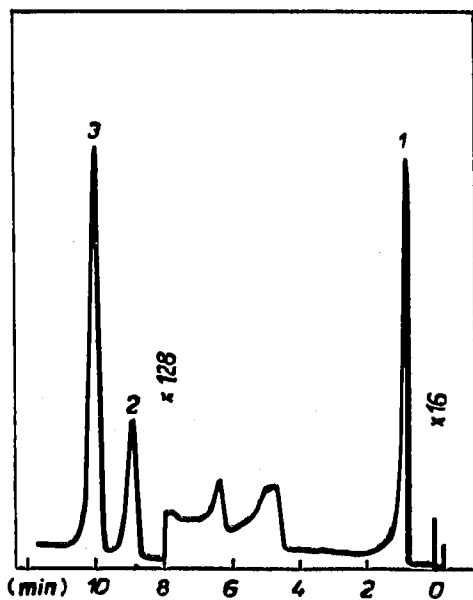


Fig. 2. Chromatogram of volatile products of cross-linking of polyethylene with dicumyl peroxide. Column 1.6 m long with 3% neopentyl glycol succinate on Chromosorb W, 0.20–0.25 mm; nitrogen inlet pressure, 0.3 kp/cm²; temperature-programmed from 80° to 180° (8.5°/min). 1 = Methane; 2 = acetophenone; 3 = α,α -dimethylbenzyl alcohol.

Fig. 3. Chromatogram of volatile products in butadiene-styrene laminates. Analysis conditions as in Fig. 2. 1 = Ethyl alcohol; 2 = toluene; 3 = styrene monomer; 4 = unknown substance; 5 = acetophenone; 6 = α,α -dimethylbenzyl alcohol.

linking by means of organic peroxides. The mechanism of this reaction was studied as follows. Polyethylene (5 mg) containing 2% of dicumyl peroxide was heated in a sealed ampoule in a nitrogen atmosphere at 140° for 8 h. After cooling the ampoule, the volatile products were analyzed by the above method (Fig. 2). Methane (1),

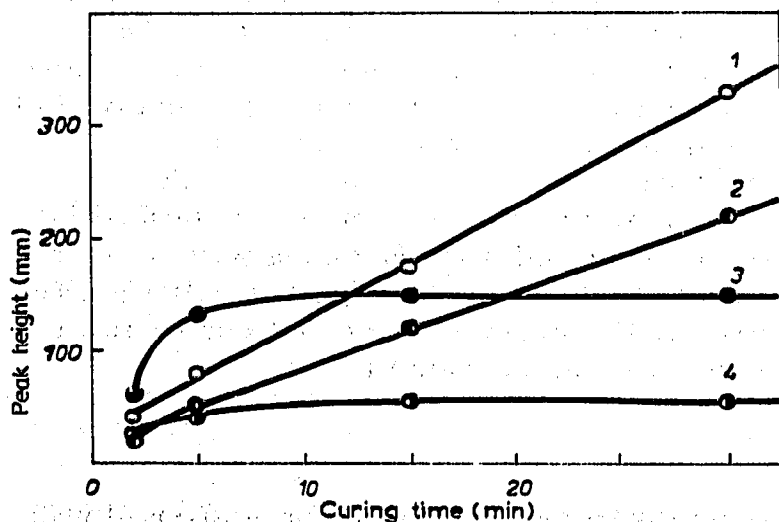


Fig. 4. Investigation of polyester-imide varnish curing by analysis of the volatile products. The graph shows the dependence of the amount of reaction products formed on the curing time. Analysis conditions as in Fig. 2. 1 = Methyl alcohol; 2 = ethylene glycol; 3 = methylphenols; 4 = dimethyl terephthalate.

acetophenone (2) and α,α -dimethylbenzyl alcohol (3) were found to be the main products of dicumyl peroxide decomposition. This result points to a complex mechanism for the decomposition of the peroxide.

Butadiene-styrene copolymer bonded laminates tend to blister during curing. We presumed that the analysis of volatile products would enable us to find the cause of this undesirable phenomenon. In our experiment, 5 mg of fine chips of cured material were sealed into an ampoule and sampled with the aid of the capillary-tip breaker heated to 180°. Under the same conditions as in the previous case we obtained a chromatogram (Fig. 3) that proves that the solvent residues of ethyl alcohol (1) and toluene (2) as well as styrene monomer (3) represent only a small part of the volatile products, the main part of which consists of the decomposition products of dicumyl peroxide-acetophenone (5) and α,α -dimethylbenzyl alcohol (6).

The polyester-imide varnish tested represented a multicomponent system, the curing of which is a complicated chemical process involving polycondensation and re-esterification reactions. We analyzed the volatile components evolved on curing the varnish in sealed ampoules, at intervals over a period of 30 min, after heating to

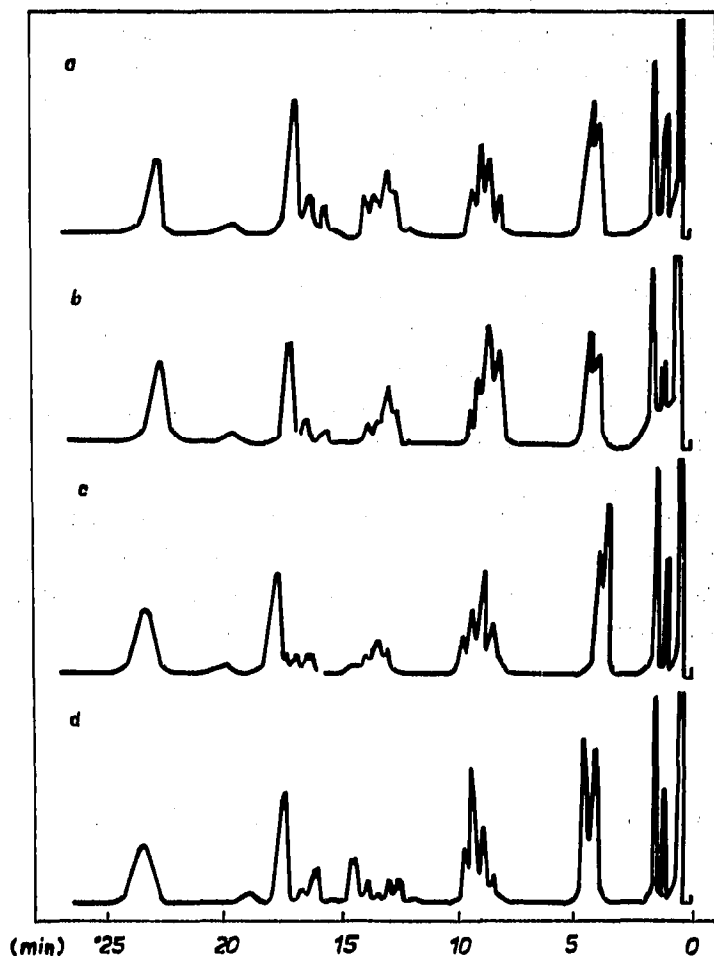


Fig. 5. Identification of polymers by pyrolysis in ampoules. Column 1.5 m long with Chromosorb 102, 80-100 mesh; nitrogen inlet pressure, 1 kp/cm²; temperature-programmed from 80 to 200° (10°/min). a = Polyethylene; b = polypropylene; c = ethylene-propylene copolymer; d = chlorosulphonated polyethylene.

250°. It can be seen from the dependences of the heights of chromatographic peaks on the curing time (Fig. 4) that the main reaction products are methyl alcohol (1) and ethylene glycol (2), while the proportions of methylphenols (3) and dimethyl terephthalate (4) remain constant, indicating that they were present in the initial material.

In the pyrolysis of polyolefins, beside characteristic low-molecular-weight, highly volatile products, high-molecular-weight products are also formed, which, on analysis by GC, considerably prolong the time required for the analysis. When pyrolysis is carried out in sealed ampoules separately from the gas chromatograph, the pyrolysis time may be prolonged arbitrarily by using a considerably lower temperature; also, it is possible to choose an arbitrary atmosphere (nitrogen, oxygen, vacuum) as required. The main advantage of pyrolysis in ampoules, however, is that on flushing the products from the ampoule at the ambient temperature of the tip-breaker, the higher-boiling substances remain in the ampoule and the analysis time is considerably shortened.

Fig. 5 shows an example of polyolefin identification by this method on analyzing the products obtained by decomposing a 1-mg sample under vacuum at 500° for 20 min. Even if the products present in all the polyolefin types mentioned are mostly qualitatively the same, they differ in quantity. It is possible on the basis of the detailed interpretation of the pyrograms, mainly in the region of elution times of about 9 min, to distinguish not only polyethylene (a) and polypropylene (b) but also their copolymer (c) as well as chlorosulphonated polyethylene (d). Other types of rubbers, polyolefins and their derivatives can also be distinguished by the same method.

CONCLUSIONS

The device developed for breaking off the ampoule tips allows the sampling of gaseous, liquid and solid substances into a gas chromatograph with several advantages. The sampling zone is prevented from contamination by non-volatile constituents, thermally unstable substances are not exposed to higher temperatures for long periods and weighing of substances for quantitative analysis and carrying out chemical reactions before analysis is possible.

Besides the potential applications mentioned above, the described system may be used for preparing volatile derivatives of low-volatile materials (esterification or silylation of acids and alcohols, pre-esterification of esters, etc.), for decomposing substances by various chemical agents and for analyzing gases occluded in polymers.

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