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PRECISION OF PYROLYSIS-GAS CHROMATOGRAPHY OF POLYMERS A PROGRESS REPORT

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CHROMATOGRAPHY SUB-GROUP COLLABORATIVE WORK

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SUMMARY

Progress of co-operative work to establish standard conditions for the pyrolysis-gas chromatography of polymers is reported. Results from "fingerprint" studies are particularly encouraging but reproducibility of quantitative results on polymer composition are disappointing.

INTRODUCTION

Late in 1968 the Gas Chromatography Discussion Group (G.C.D.G.) of the Institute of Petroleum formed a pyrolysis-gas chromatography (PGC) sub-group. The objectives of the sub-group included the rationalisation and standardisation of PGC. It was felt that, whilst the technique was proving to be very successful both as a fingerprint technique and for quantitative analysis in many individual laboratories, because of the wide diversity of pyrolysis and chromatographic conditions inter-laboratory correlations were non-existent. It was hoped that by standardising operating conditions, at the very least fingerprint pyrograms of commercial polymers could be obtained reproducibly. By publication of such fingerprints in a standard format the work of calibration in the many interested laboratories could be radically reduced.

The sub-group's first activity was to circulate a fact-finding questionnaire which sought information on methods of pyrolysis and of GC employed, sample types studied, views on defects of present technology and objective of doing PGC (*i.e.* for fingerprinting and for quantitative analysis, for example). The replies have been summarised¹. They showed, as expected, a wide diversity in methods used, a fairly general dissatis-

faction with the precision of PGC, a predominant interest in the study of commercial polymers and a welcome willingness to collaborate in work to improve the technique. Accordingly a preliminary programme was undertaken which commenced early in 1969, three polymers being distributed. Participating laboratories were asked to obtain both qualitative and quantitative data on them. For the sake of expediency, this work was confined to laboratories in Great Britain. Full details of this programme are given later and the purpose of this paper is to record the results obtained, draw conclusions from them and to pinpoint the way ahead.

EXPERIMENTAL

Programme

The programme agreed required that co-operating laboratories pyrolysed three samples, provided by Vinyl Products, by any or all of the normal procedures used in each participants laboratory. The pyrolysis products were to be separated on columns packed with stationary phases provided by Perkin-Elmer. The two phases provided were (i) 10% Apiezon L on 80-100 mesh Chromosorb W; and (ii) 10% ethylene glycol-adipic acid polyester on 80-100 mesh Chromosorb W. The column and detector operating conditions, as well as the conditions for pyrolysis, were left to the discretion of individual laboratories.

The samples circulated were: (i) bulk-polymerised styrene homopolymer, triple precipitated (specially prepared by Vinyl Products); (ii) styrene-butadiene block copolymer (commercial product); styrene content was 24.5 wt. % authenticated by other methods; and (iii) methyl methacrylate-styrene-butadiene terpolymer (commercial product).

The information sought on these samples was as follows. Samples (i) and (ii): a pyrogram and estimated styrene monomer recovery (to be obtained by pyrolysing completely a known weight of sample and calibrating detector response with pure monomeric styrene). Sample (iii): fingerprint pyrogram only.

Summary of actual operating conditions used in the programme

Eighteen laboratories reported results, some using more than one pyrolysis technique and most using both of the stationary phases provided. Actual conditions employed varied considerably; the following tabular summaries give an indication of the range of methods used (Tables I-III).

TABLE I

METHOD OF PYROLYSIS AND NUMBER OF LABORATORIES USING PARTICULAR PYROLYSIS TECHNIQUES

<i>Technique</i>	<i>Number using</i>
Commercial filament	6
Home-made filament	4
Curie-point system	7
Commercial furnace	1
Home-made furnace	2

TABLE II

CONDITIONS OF PYROLYSIS; VARIATIONS IN MOST SIGNIFICANT OPERATING PARAMETERS

Temperature (°C)	400-770
Time of pyrolysis (sec)	2-15
Sample size (μg)	1.5-2000

TABLE III

GC COLUMN OPERATING CONDITIONS

Carrier gas flow rates 20-90 ml·min⁻¹

	Number of laboratories	Temperature range	
		min. (°C)	max. (°C)
Isothermal	16	50	150
Programmed	2	50	→ 250

QUANTITATIVE RESULTS

Styrene homopolymer

Recovery of styrene as monomer ranged from 26-102 wt. % and is recorded in histogram form in Fig. 1. Of note are the differences reported from a particular laboratory between the two columns as shown in Table IV.

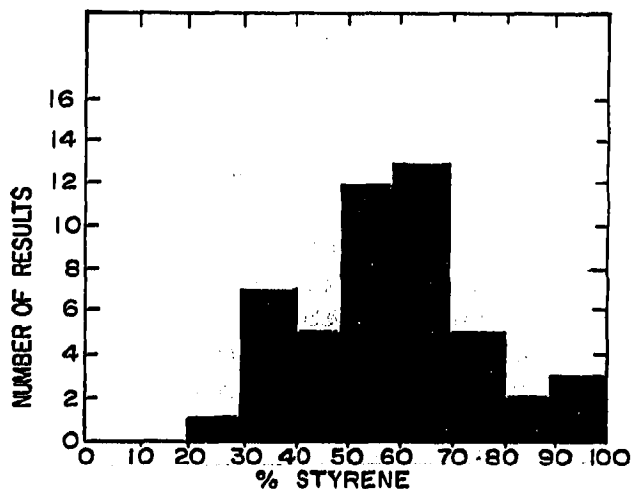


Fig. 1. Styrene recoveries.

Styrene-butadiene block-copolymer

The styrene content was determined to be anything between 9 and 41 % (although actually 24.5 % the maximum yield is about 21 %).

TABLE IV

STYRENE RECOVERIES (WT.%)

Laboratory	Apiezon L	Polyester
1	55	80
2	62	67
3	92	65
4	{ 78 ^a 88 ^a	{ 102 ^a 98 ^a

^a Duplicate results reported from a single laboratory.

DISCUSSION OF QUANTITATIVE RESULTS

The results of the test have to be considered in the light of the objectives behind the circulation of each of the three samples.

The objective of examining the styrene homopolymer was to establish to what extent the different pyrolysis conditions led to depolymerisation, since it was considered possible that conditions which led to approaching 100% monomer yield would be those which favoured repeatable, and reproducible, pyrolysis of polymers in general. This view is as yet unsubstantiated by factual evidence. The results of this work revealed a considerable variation in monomer yield; it is suggested that this reflected a combination of unsatisfactory pyrolytic conditions and also, and probably more significantly, non-quantitative pyrolysis and subsequent transfer of pyrolysate from pyrolysis zone to detector. Even more striking was the very considerable difference in monomer recovery reported by several laboratories between work with the APL and PEGA columns. These discrepancies have so far eluded explanation.

The quantitative determination of styrene content of the copolymer was sought as an indication of the "reproducibility" of PGC. The results (between 9 and 41%) for a sample known to contain 24.5% speak for themselves. At the present time, except within a single laboratory or between a group of laboratories which have rigidly standardised conditions, precision is exceedingly poor and even in the more favourable circumstances mentioned accuracy may also be intolerably bad.

FINGERPRINT ASSESSMENT

The very wide range of operating temperatures, flow rates, chart speeds and attenuation settings made the visual assessment of the submitted pyrograms very difficult. Without prior knowledge of the material pyrolysed and the separating column used, comparison of the pyrograms would undoubtedly have been an extremely long task. Even when classified a large variation appeared within each set. The three examples shown in Fig. 2 (SBR on APL) give some idea of the variation of pattern encountered. Even with foreknowledge it is difficult to accept that these are from the same material.

After close inspection of the sets of chromatograms it was apparent that the few patterns obtained by temperature programming were so different from those obtained using isothermal conditions that further assessment was restricted to the isothermal data. There was no apparent correlation between the patterns obtained and

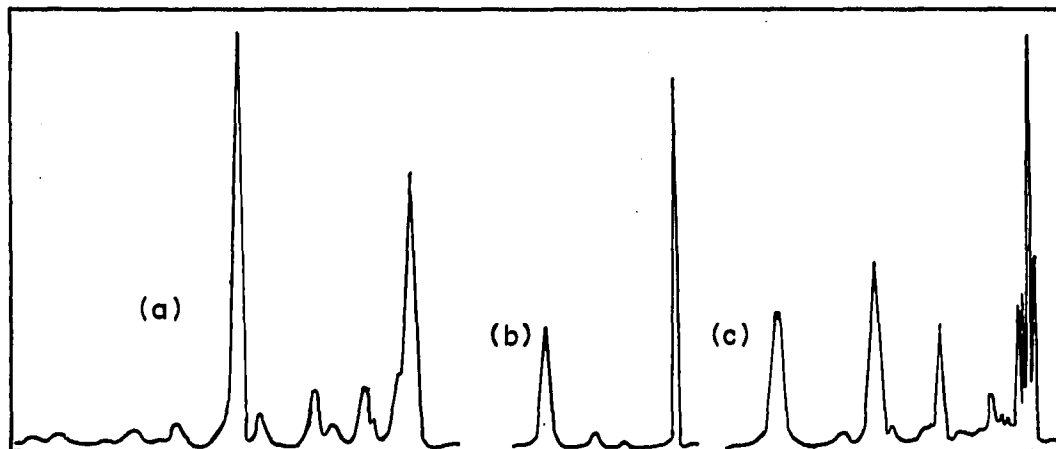


Fig. 2. Three examples of pyrograms obtained from SBR using APL columns (a) programmed $50^{\circ} \rightarrow 200^{\circ}$ (b) and (c) isothermal 80° .

the type of pyrolysis unit used or the pyrolysis temperature but the variations in pattern due to other causes were so large that any such differences might have been masked.

In order to decide the value of the isothermal patterns, attempts were first made to classify the major peaks by retention distance and area. Retention data proved to be unsatisfactory as most of the pyrograms did not give any indication of the injection point or dead volume. Area measurements produced as wide a range of results as those shown earlier for the styrene homopolymer. At this stage it was quite clear that assessment would have to be purely visual.

In an attempt to eliminate the variables introduced by attenuation, temperature, flow rate and chart speed, selected pyrograms from the SBR and the terpolymer were re-drawn so that the distance between the first peak on the pyrogram and the styrene peak was standardised. Where possible all peaks were redrawn to a common attenuation. Once this was done the classification was simple and the similarity between the patterns in any set was immediately obvious. Examples of redrawn pyrograms are shown in Fig. 3. The differences in peak height and relative retention are readily accommodated by the eye.

CONCLUSIONS AND FUTURE WORK

The results obtained to date substantiate the view (generally supported by respondents to the Group's original questionnaire) that PGC techniques leave much to be desired, particularly with respect to precision. Unfortunately the quantitative results do not enable one to reach any conclusion on a preferred method of pyrolysis; for example results obtained with Curie-point pyrolysers and microsamples, widely believed to offer the best hope for reproducibility, are as bad as those obtained by other means.

Fingerprinting the polymers for qualitative purposes was a far more encouraging exercise and, as has been shown, it gave fairly good pyrogram reproducibility once the pyrograms had been rationalised.

In these circumstances it is recommended that the Sub-Group concentrates

its energies on polymer fingerprinting, where the auguries for building up a library of reproducible pyrograms are good. For further co-operative programmes it is felt that a standard operating temperature should be adopted by all laboratories and that an attempt should be made to produce pyrograms with a specific peak at a specified distance from the origin; gas flow rate and/or chart speed could be varied to this end. Such presentation would greatly facilitate the visual assessment of the pyrograms and extend their use for reference purposes.

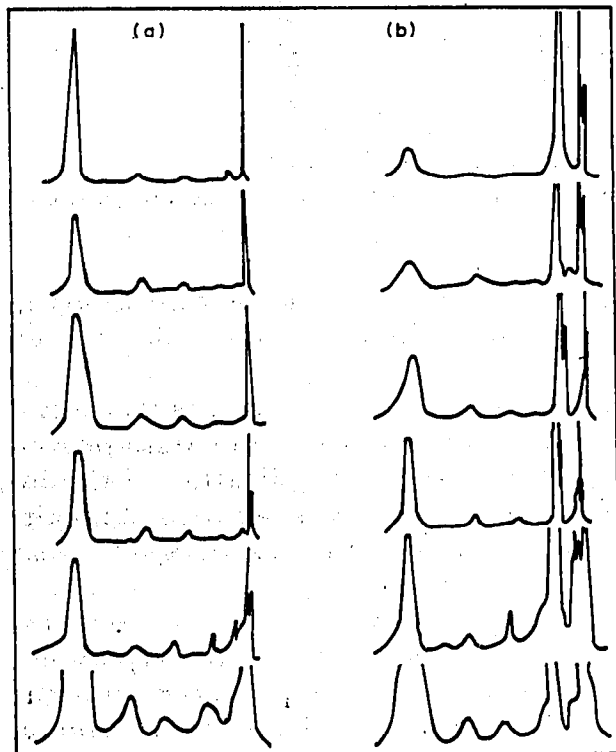


Fig. 3. Redrawn pyrograms (a) SBR and (b) terpolymer.

Detailed proposals for a second programme, devoted to fingerprinting commercial polymers, are in hand and have been discussed with likely participants. In the meantime the officers of the Sub-Group wish to acknowledge the great help given by individuals and laboratories too numerous to mention here.

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REFERENCE

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