Multichannel Autosampler for Curie-Point Pyrolysis Capillary Gas Chromatography

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Summary

A multichannel autosampler which can automatically analyze up to 20 samples h sequence has been developed for on-line Curie-pout pyrolysis - capillary GC. The results obtained from the system show that the analysis of thermally labile samples could be performed without either thermal degradation or reaction during the waiting time before the final pyrolysis. The reproducibilities of the relative peak areas and retention times of the characteristic pyrolysates of a tricomponent copolymer were significantly better than those obtained by manual sample manipulation.

1 Introduction

Pyrolysis is used as a means of sample introduction for the gas chromatographic analysis of high molecular weight compounds: the technique uses high temperatures to degrade the compounds to a characteristic mixture of volatile monomers. oligomers, and other pyrolysates. Curie-point pyrolysis - capillary GC is a powerful method for analysis of the composition and structure of such non-volatile compounds as syntheticplastics [1]. rubbers [2]. and paints [3].

In previous work. liquid, solid, and powder samples have been handled by wrapping in 50μ m thick Pyrofoil®, placed in a specially developed. magnetic. metal foil holder. and inserted into the pyrolyzer [4. 5]. Because pyrolysis can be effected by a number of experimental parameters. it should be performed as reproducibly as possible. especially for quantitative analysis. For this reason we have developed a multichannel autosampler which can handle up to 20 samples without causing any degradation and/or further polymerization inside the sample holder during the waiting time before final pyrolysis. This has solved a problem observed with another autosampler [6] in which thermally labile compounds could be degraded or polymerized before pyrolysis [7. 8].

The results from quantitative analysis of multi-component polymers has shown that as a result of the standardization of experimental conditions the reproducibility obtained using the autosampler is much improved in comparison with manual sample manipulation.

2 Experimental

2.1 Instrumentation

A schematic diagram of the model JPS-220 multichannel autosampler and JHP-22 pyrolyzer is shown in **Figure 1**. Samples are weighed and individually wrapped in Pyrofoil@ in a manner ensuring good contact. The Pyrofoil@-wrapped samples (A) are placed on a magazine (B). the purge valve (C) opened to replace the air inside the equipment with carrier gas. and, after 1 min. the six-port valve (D) turned to the sampling position. The first sample is pushed by the injector (E) down to a pyrolysis chamber (F) where it is instantaneously pyrolyzed. The pyrolyzates are transferred, through (D), to a on-line GC column for chromatography.

A magnet (G) is then lowered to retrieve the spent sample and returned to the upper position. A slide-way (I) is placed below the magnet and when the electricity supply to the magnet is switched off the used sample (H) slides into the trap (J). The slide is then returned to its initial position. The instrument is controlled by unit (K).

When gas chromatographic analysis of the first sample is complete. the foil magazine is moved forward. the second sample dispensed into the pyrolysis chamber by the plunger. and the second processing begins automatically. This sample introduction method is repeated up to 20 times from one magazine.

In order to keep the carrier gas flow rate constant. during operation the inlet gas pressure is controlled by a pressure balancer (L). Without this pressure controller. it took more than 30 min to obtain the stable gas pressure which is important for production of reproducible pyrograms.

2.2 Condition for Pyrolysis GC

About 0.2 mg of a sample. wrapped in Pyrofoil, was heated at 590 for 3 s The sample introduction and pyrolysis system were coupled directly to a model HP 5890A gas chromatograph (Hewllet-Packard) equipped with a model D-2520 integrator (Hitachi). The GC system was equipped with name ionization detection and fitted with a 30 m x 0.25 mm id. fused silica
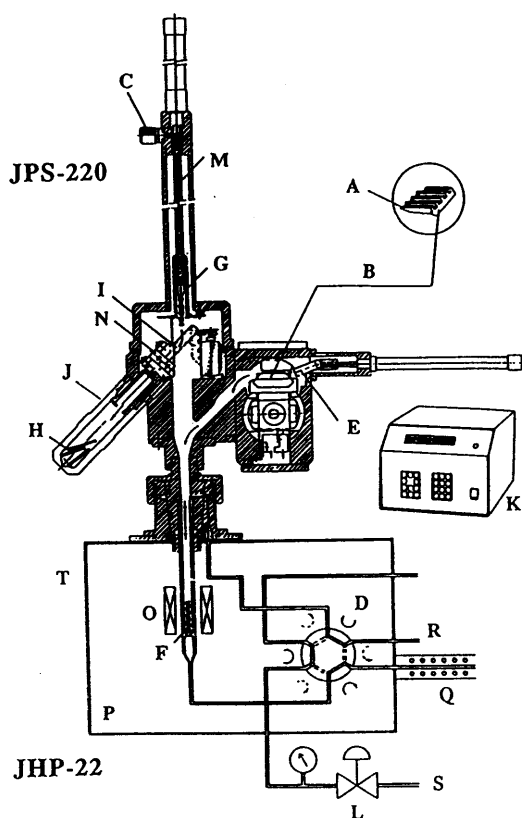
Figure 1

The JPS-220 multichannel autosampler coupled with the JHP-22 Curie-point pyrolyzer: A, Pyrofoil®-wrapped sample; B, magazine; C, purge valve; D, six port valve; E, injector; F, pyrolysis chamber; G, foil collection magnet; H, used samples; I, slide way; J, trap for used samples; K, controller; L, pressure balancer; M, foil collection shaft; N, photosensor; O, radio frequency coil; P, sample tube; Q, transfer pipe coupled to GC; R, carrier gas inlet; S, gas inlet for pressure balancing; T, oven.

capillary column coated with a 0.25 μ m film of immobilized polydimethylsiloxane (DB1: J&W. Folsom. CA. USA).

Following pyrolysis, the column temperature was maintained at 50 for 3 min and then programmed at 10° /min to 250 which was held for 10 min. Helium was used as carder gas: a total flow rate of 50 ml/min was split in the ratio 50 : 1. The identification of the pyrolysates was performed with a directly coupled model QP 2000 A quadrupole mass spectrometer (Shimadzu): ionization was by EI at 70 ev.

2.3 Samples

A commercial bisphenol A type epoxy prepolymer and modified polyamide hardener were obtained from Konishi. A Toyolac 700 ABS resin. a copolymer of acrylonitrile (23 %). butadiene (13 %). and styrene (64 %). was obtained from Toray lndustries.
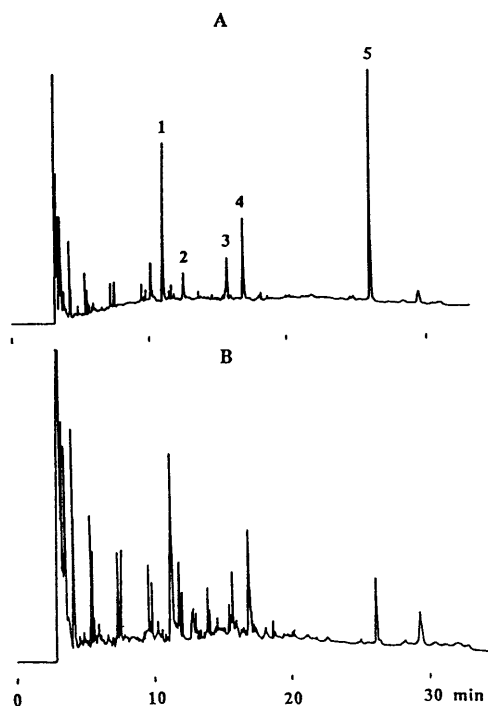

Figure 2

Pyrograms of (A) uncured epoxy resin mixed with amide hardener at room temperature and stored in the sample magazine for 1 to 60 min, and (B) the epoxy resin cured at 150 °C for 1 h: 1, phenol; 2, cresol; 3, p-isopropylphenol; 4, p-isopropenylphenol; 5, bisphenol A.

3 Results and Discussion

The multichannel autosampler coupled on-line with the Curie-point pyrolyzer and the capillary GC system may be used not only for time-saving automatic measurements on a large number of samples, but also for the highly accurate quantitative analysis of thermally labile samples.

3.1 Anarysis of a Thermally Labile Sample

Conventional autosamplers for pyrolysis GC are usually provided with auxiliary heating in order to maintain the sample holder at a temperature sufficient to prevent condensation of pyrolysates on its inner wall [6]. Because uncured epoxy resins are susceptible to further curing. even at low temperatures. when such samples are mounted in a conventional pyrolyzer they are often exposed to temperatures which cause further curing during the waiting period before final pyrolysis: the degree of reaction depends on the temperature, the waiting time. and the size of the sample. etc.: these are. in turn. reflected in the specificity and the reproducibility of the resulting pyrograms [8].

Since the sample magazine of JPS-220 is designed to be located far from the pyrolysis chamber. such heating is not necessary. This enables thermally labile samples to be analyzed reproduci-
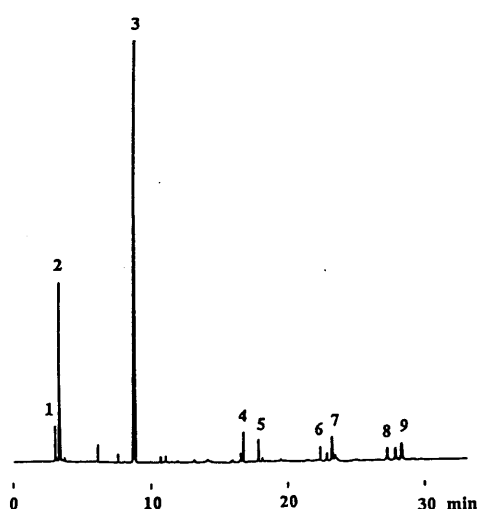
Figure 3

Pyrogram of ABS (acrylonitrile – butadiene – styrene) copolymer:
1, B; 2, A; 2, S; 4, AS; 5, SA; 6, SS; 7, ASA; 8, ASS; 9, SAS.

bly. **Figure 2A** shows the pyrogram obtained from a sample of the epoxy resin mixed with amide hardener (1:1) at room temperature. No changes were observed in the pyrograms when samples were stored in the sample magazine from 1 to 60 min. which indicates that the JPS-220 is suitable tor the analysis of thermally labile samples. The pyrogram of the epoxy resin cured at 150 for 60 min is shown in **Figure 2B**: compared with the

pyrogram from the uncured resin some of the monophenol pyrolysate peaks had increased in size whereas that of bisphenol A had, in contrast. decreased. These differences obviously reflected the curing reactions of the epoxy resin with amide-hardener.

3.2 Reproducibllity

The reproducibility of PY-GC analysis is influenced by each of a series of steps: one of the most critical is the sample handling technique [9]. As already mentioned. the use of an autosampler enables reproducible sampling handling: because of this an enhancement of the reproducibility and standardization of quantitative analysis would be expected.

A tricomponent copolymer, art ABS resin. was analyzed quantitatively using both automated and manual sample introduction systems. **Figure 3** shows the pyrogram of the ABS resin: the intensities of the monomer (A. B. and S). dirner (AS. SA, and SS) and trimer (ASA. ASS. and SAS) peal(s represent the structural specificity and composition of the copolymer.

The relative peak areas and retention times of the specific pyrolysates are summarized in **Tables 1** and **2**. respectively The relative standard deviations (CV%) of the peak areas and retention times (t_r) are also listed in the tables and (in part) presented schematically **Figure 4**. The CV% and t_r data show that the experimental reproducibility obtained using the autosampler were as much as 1.3 and 2.3 times better, respectively. than those obtained by manual sample introduction under the same conditions.

We consider that in addition to the completely uniform sample introduction, pyrolysis. and chromatographic processing effected by the autosampler control. there is another reason for this improvement: the removal of air by purging the pyrolyzer with carrier gas. During manual sample introduction, air enters the

Table 1

Reproducibility of relative peak areas of the characteristic pyrolysates of an ABS coploymer.

No.	Relative peak areas Monomer			Dimer			Trimer		
	B	A	S	AS	SA	SS	ASA	ASS	SAS
JPS-220 multichannel autosampler									
1	2.11	12.54	65.16	3.32	2.89	2.37	4.79	2.67	4.10
2	2.03	12.10	66.25	3.41	2.75	2.29	4.60	2.54	3.85
3	2.17	12.36	66.46	3.28	2.70	2.02	4.46	2.58	3.93
4	2.02	12.06	66.31	3.43	2.78	2.27	4.50	2.51	3.90
5	1.81	11.47	67.22	3.72	2.72	2.45	4.54	2.32	3.71
Average	2.03	12.10	66.28	3.43	2.77	2.28	4.58	2.52	3.90
CV%	6.7	3.4	1.1	5.0	2.7	7.1	2.8	5.1	3.6
Manual sample handling									
1	2.17	12.46	65.30	3.22	2.80	2.43	4.33	2.43	4.81
2	2.11	12.70	69.41	3.16	2.70	2.25	2.99	1.71	2.88
3	2.05	12.00	71.14	2.80	2.42	2.02	2.61	2.30	2.53
4	1.45	10.96	65.34	3.30	2.80	2.69	3.91	3.32	6.19
5	1.73	11.62	70.28	2.91	2.13	1.78	2.35	1.82	5.32
Average	1.90	11.95	68.29	3.08	2.57	2.23	3.24	2.32	4.35
CV%	16	5.8	4.1	6.9	11	16	26	28	36

Table 2

Reproducibility on retention times of the characteristic pyrolysates of an ABS copolymer.

No. Retention time of pyrolysate [min]									
Monomer			Dimer			Trimer			
B	A	S	AS	SA	SS	ASA	ASS	SAS

JPS-220 multichannel autosampler

1	3.17	3.43	8.96	16.95	18.09	22.61	23.51	27.60	28.69
2	3.08	3.33	8.81	16.77	17.90	22.40	23.28	27.31	28.36
3	3.08	3.32	8.71	16.66	17.80	22.36	23.23	27.29	28.35
4	3.19	3.45	8.91	16.85	17.99	22.49	23.38	27.44	28.51
5	3.16	3.41	8.83	16.78	17.91	22.42	23.28	27.33	28.38
Average	3.13	3.38	8.84	16.80	17.93	22.45	23.33	27.39	28.45
CV%	1.7	1.8	1.1	0.6	0.6	0.4	0.5	0.5	0.5

Manual sample handling

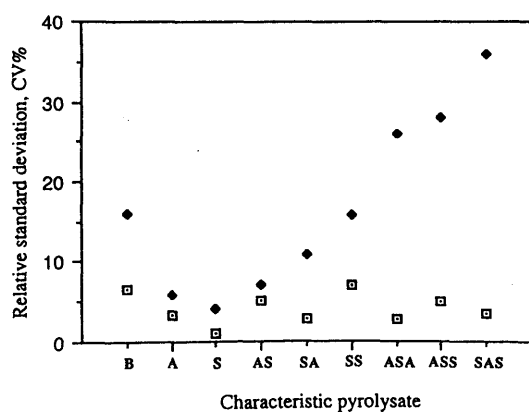|									
1	3.68	3.97	9.71	17.83	18.99	23.65	24.57	29.02	30.23
2	3.58	3.87	9.57	17.64	18.80	23.41	24.33	28.71	29.89
3	3.48	3.76	9.43	17.47	18.62	23.20	24.10	28.41	31.65
4	3.26	3.53	9.15	17.18	18.56	22.87	23.77	27.95	29.08
5	3.24	3.51	9.15	17.15	18.29	22.83	23.73	27.92	29.03
Average	3.44	3.72	9.40	17.45	18.65	23.19	24.10	28.40	29.97
CV%	5.6	5.5	2.7	1.7	1.4	1.5	1.5	1.7	3.6

Figure 4

Relative standard deviation of peak areas of characteristic pyrolysates of ABS resin obtained by pyrolysis GC with automated (□) and manual (♦) sample introduction.

pyrolyzer to varying degrees and this reduces the quantitative reproducibility of the analysis. This problem is almost eliminated by use of this autosampler.

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