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Qualitative analysis of a commercially available phenol–formaldehyde resin, by static and dynamic headspace analysis using a mass-selective detector

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ABSTRACT

Static headspace and dynamic headspace procedures for volatile substances in solid matrices were investigated and compared by gas chromatography–mass spectrometry (GC–MS). For this purpose volatile components of a commercially available phenol–formaldehyde resin were analysed by GC–MS, first using the traditional static headspace method. A further study of the method aimed at obtaining a greater concentration, together with increased selectivity and a more reliable structural determination of the volatile substances, led to the use of the dynamic headspace (purge and trap) method. Following the latter method, after enrichment, the trap contents were recovered in solvents with different polarities in order to concentrate selectively the substances contained in the vapours of the resin itself. The solutions obtained were analysed by GC–MS.

INTRODUCTION

Volatile organic compounds in solid matrices can be analysed by gas chromatography (GC) using the static headspace and dynamic headspace (purge and trap methods)[1–3]. The former method consists in heating the solid matrix in a hermetically closed vessel. The gaseous phase is analysed after a certain periode once equilibrium has been reached. The results are thus interpreted as a description of the gas–solid system at determined pressure, temperature and volume values (analysis of the thermodynamic equilibrium system). In the dynamic headspace method, the sample is prepared using the same procedure as in the former method and is swept by an inert gas stream (helium) that conveys the gaseous volatile compounds to a cold trap usually kept at a temperature 30–40°C lower than the retention temperature of the substance to be detected. The trap is filled with a solid phase (e.g., Tenax TA, graphitized carbon, SE-30, OV-1 on Chromosorb, etc.). After rapid heating, the stripping gas from the trap is carried into a gas chromatograph for analysis.

Sometimes the gas flow required both to wash the trap thoroughly and to allow for well resolved chromatographic peaks cannot be injected directly (split or splitless)

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into the capillary column. One can then operate according to one of two procedures. In one, collect all stripping gas in a 0.53-mm empty and passivated/silanized fused-silica wide-bore capillary, about 20 cm long, kept at low temperature under liquid nitrogen. Insert the capillary tube in a split/splitless injector and heat it quickly under an inert gas flow. Adjust the analysis parameters according to the type of capillary column being used. In the other, immerse the purge and trap outlet capillary tube in a few millilitres of pure polar or apolar solvent maintained at a low temperature and allow the stripping gas to bubble in the liquid. It can be immediately understood why the latter method can only be used for qualitative analyses. Both the bubbling (small bubbles with as long a time of bubble–solvent contact as possible) and solvent evaporation phases are critical. Decreasing the final volume with respect to the initial volume would bring about a proportional increase in the impurities likely to be present in the blank.

The main advantage of the dynamic over the static headspace method is the wider range of substances that can be detected. This derives from the fact that the vial washing gas carries a greater amount of components towards the trap and thus to the detector used (non-equilibrium system analysis).

EXPERIMENTAL

The solid matrix on which tests were performed is a common phenol–formaldehyde resin. Such a resin contains a wide range of compounds obtained from the condensation reaction of phenols or substituted phenols with aldehydes. Resolic resins are obtained when operating with an excess of aldehyde and a basic catalyst (ammonia, sodium hydroxide solution), whereas novolak resins are obtained when there is an excess of phenol under acidic conditions. *para*-Alkyl-substituted phenols produce water-soluble liquid linear resins (mol. wt. 125–150) or organic solvent-soluble solid resins (mol. wt. > 1000). The use of molten resin as raw material or as a co-blender in polymeric matrices promotes irritating, corrosive and foul-smelling vapours, even if used at relatively low temperatures (80–100°C).

Apparatus and conditions

The gas chromatograph was an HP 5890 (Hewlett-Packard) with an HP 5970 mass-selective detector in the total ion current mode. The transfer line was maintained at 280°C. The inlet type was split only or splitless. The mass range was 33–350 U. The split operating mode was used. The oven temperature was programmed from 40 to 250°C at 8°C/min. The column was 12 m × 0.2 mm I.D. coated with Ultra 2 fused silica (Hewlett-Packard) (cross-linked 5% phenyl methyl silicone), with a 0.32-μm film thickness. The carrier gas was helium (SIO-Alphagaz, N60 type, purity $\geqslant$99.9999%) with a column head pressure of 50 kPa and a split vent of 60 cm^3/min. The sample was 0.2 ml (static headspace method) or 2 μl (dynamic headspace method). An HP 59970 MS Chemstation Rev. 3.2 data station installed on an HP 9000 Series 300 was used.

For the dynamic headspace (purge and trap method) a Dani SPT 37.50 equipped with a Dani constant incubation time (CIT) device was used (Fig. 1). A constant-temperature bath was maintained at 130°C (silicone oil) and the temperature of the switching valve and transfer line was 135°C. The incubation time was 2 or

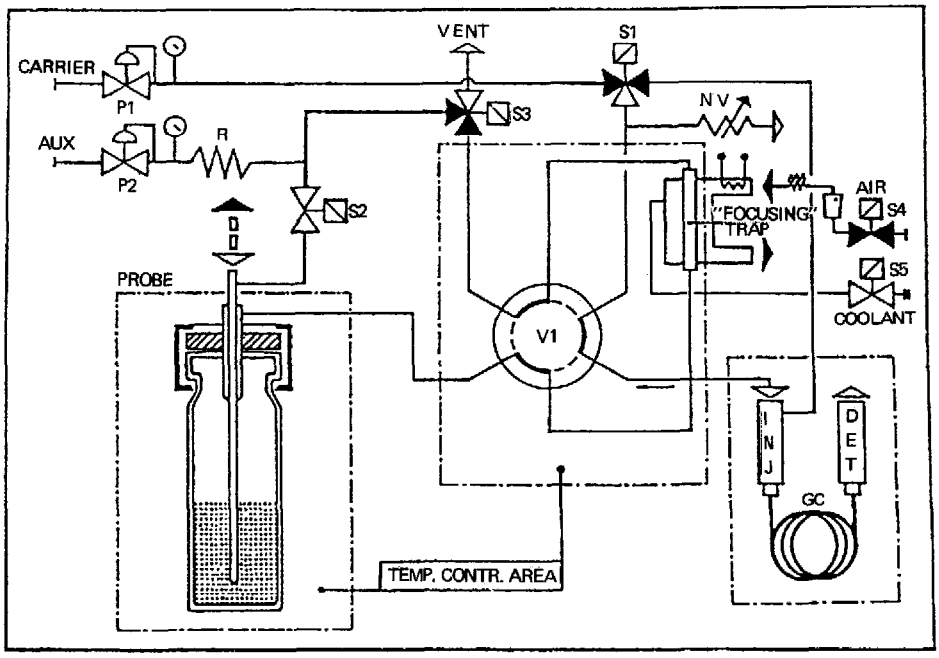

Fig. 1. Dani SPT 37.50 pneumatics scheme. P1, P2 = pressure regulators; S1–S5 = solenoid valves; NV = needle valve; R = calibrated restrictor; V1 = six-port pneumatic valve; INJ = injection: DET = detection; TEMP.CONTR. = temperature-controlled.

24 h. The trap packing was 200 mg of Tenax TA (60–80 mesh) and the trap temperature was increased from 30 to 300°C at 1200°C/min. The cooling time was 4 min, purging time 3 min, trap desorption time 2 min and trap back-flushing time 4 min (2 h after each analysis set) at 300°C.

Reagents

Methanol (HPLC grade) was obtained from Carlo Erba. A 0.01 *M* solution of sodium hydroxide in distilled water was prepared. SP 1045 resin (Schenectady Europe) (mol. wt. > 1000) was used.

RESULTS AND DISCUSSION

Static headspace analysis

Two resin samples were prepared in 40-g sealed glass containers with silicone septa. After preconditioning at 130°C (2 h for the first sample, 24 h for the second), 0.2 ml of gas phase was injected into the GC–mass spectrometry (MS) system (see Figs. 2 and 3). On comparing the two chromatograms obtained, it was found that after 24 h the following appeared: methanoic acid (Table I, peak 1), phenol (12), diethylstilbestrol (30) and 2,4-(1,1,3,3-tetramethylbutyl)diphenol (34). Further, there is a decrease in 4-(1,1,3,3-tetramethylbutyl)phenol (31). The analysis performed after conditioning for only 2 h at 130°C showed a non-equilibrium system (Fig. 3), whereas the second analysis showed a thermodynamic steady equilibrium system. In fact, after

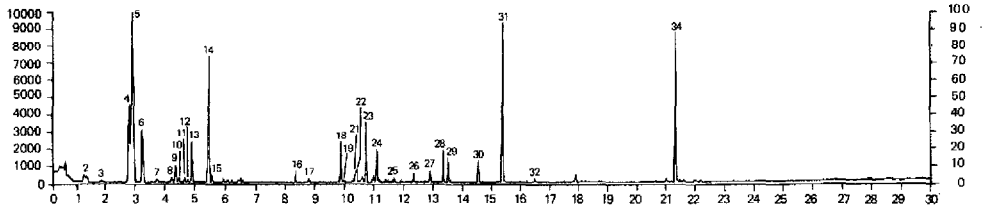

Fig. 2. Resin after 2 h at 130°C. Static headspace method.

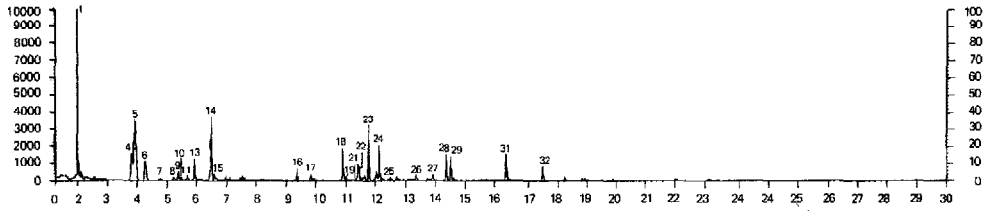

Fig. 3. Resin after 24 h at 130°C. Static headspace method.

TABLE I

IDENTIFIED PEAKS IN FIGS. 2–6

Peak No.	*Compound*[a]	*Peak No.*	*Compound*
1	Methanoic acid	20	1,2-Diaminobenzene
2	5,5-Dimethyl-2-hexene	21	4-(1,2-Dimethylethyl)phenol
3	4,4-Dimethyl-2-pentanone	22	Cyclohexane, substituted
4	Ethylbenzene	23	1-Propene-2-methyl-, tetramer
5	1,3-Dimethylbenzene + 1,4-dimethylbenzene	24	1-Propene-2-methyl-, tetramer
6	1,2-Dimethylbenzene	25	2,5-Bis(1-methylethyl)phenol
7	(1-Methylethyl)benzene or isopropylbenzene	26	4,4-Dimethyl-1-ethoxy-2-pentene
8	1-Methyl-*x*-ethylbenzene	27	Heptyl hexyl ether
9	1-Methyl-*x'*-ethylbenzene	28	1-Ethyl-*x*-(1,1,3,3-tetramethylbutyl)benzene
10	1-Methyl-*x''*-ethylbenzene	29	1-Ethyl-*x'*-(1,1,3,3-tetramethylbutyl)benzene
11	1,2,4-Trimethylbenzene	30	Diethylstilbestrol
12	Phenol	31	4-(1,1,3,3-Tetramethylbutyl)phenol
13	1,2,3-Trimethylbenzene	32	2-Ethyl-4-(1,1,3,3-tetramethylbutyl)phenol
14	1-Methyl-3-(1-methylethyl)benzene	33	1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl) ester
15	2-Ethyl-1-hexanol	34	2,4-(1,1,3,3-Tetramethylbutyl)diphenol
16	1,4-Bis(1-methylethyl)benzene	35	4,4'-Oxydianiline
17	1-(1,1-Dimethylethyl)-3,5-dimethylbenzene	36	[1,1':3',1''-Terphenyl]-2'-ol
18	1,1,3,5-Tetramethylcyclohexane	37	[1,1'-Phenoxy:3',1''-bisphenyl]-2'-ol
19	4-(1,1-Dimethylethyl)phenol	*	Column bleeding

[a] x = Uncertain positions of substituents ($x \neq x' \neq x''$)

40 h, the same results were also achieved and a similar chromatogram was obtained (not shown).

Dynamic headspace analysis

Two sets of phenolic resin samples (three vials for each) were prepared with a total weight of 40 g per set. Preconditioning was performed inside the Dani SPT 37.50 instrument in a suitable silicone-oil bath maintained at a 130°C for 2 and 24 h for the first and second set of samples, respectively. After the conventional purging and trapping phases, the washing gas for each vial was allowed to bubble into 0.5 ml of methanol kept in a Dewar vessel containing solid carbon dioxide. After each set of three vials, the trap was left to backflush at 300°C for 2 h. A 2-μl aliquot of the collecting vessel contents was injected into the GC–MS system (see Figs. 4 and 5).

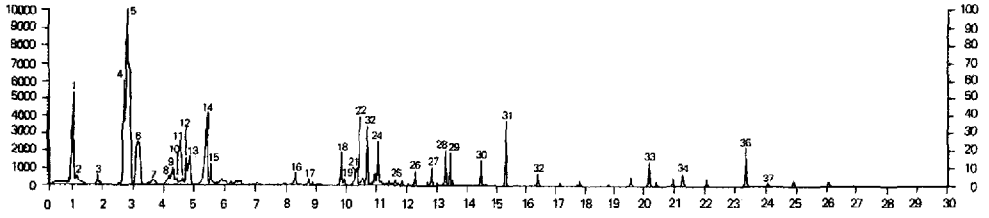

Fig. 4. Resin after 2 h at 130°C. Dynamic headspace method (methanol).

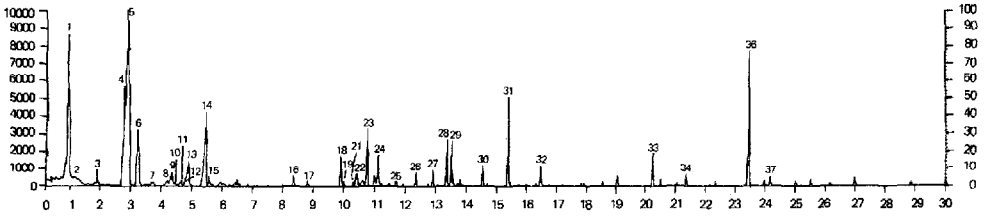

Fig. 5. Resin after 24 h at 130°C. Dynamic headspace method (methanol).

Interpretation of the mass spectra of the peaks allowed an approximate identification of the resin components. However, in many instances the exact identification of a component proved difficult owing both to an insufficient GC selectivity and to the fact that the amount involved was too small to give an easily identifiable mass spectrum. A new set of samples was therefore prepared. After their preconditioning at 130°C for 24 h, the trap eluate was collected in 0.5 ml of 0.01 *M* sodium hydroxide solution kept at 0°C in an ice–water bath. In this manner the substituted phenols (main responsible for the imperfect peak splitting) remained in solution as anions in equilibrium with the uncharged form. A slight helium flow for a few minutes was sufficient to remove the traces of hydrocarbons and insoluble apolar components. A chromatogram containing peaks almost all of which are due to polar compounds (see Fig. 6) and comparison of the chromatograms shown in Figs. 2–6 to one another, made it possible to identify 38 different compounds (see Table I). As described in the Introduction the two chromatograms in Figs. 4 and 5 clearly represent a non-equilib-

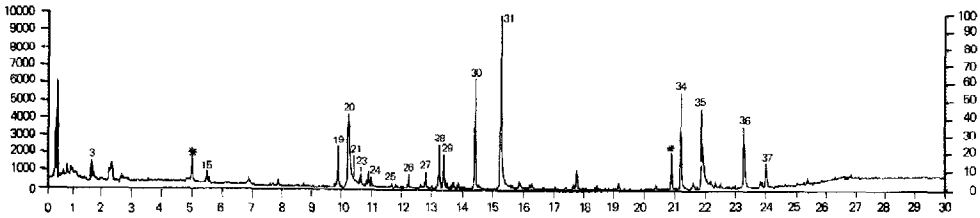

Fig. 6. Resin after 24 h at 130°C. Dynamic headspace method (water).

rium system. The only difference, probably ascribable to slower desorption kinetics from the molten matrix, is a marked increase in some heavy fractions (peaks 36 and 37). Fig. 6 shows two peaks that were not observed in the previous analyses, *i.e.*, 20 and 35. These amine compounds are probably due to the type of catalyst used in the resin synthesis *i.e.*, ammonia or an organic amine.

CONCLUSIONS

Upgrading various operating parameters makes it possible to determine most impurities in a solid matrix. Obviously, a more in-depth characterization could provide a broader picture. To achieve such detail one must operate with traps filled with different phases (*e.g.*, Carbotrap) kept at low temperatures (liquid nitrogen cooling), directly inject the purge and trap eluate into the capillary column or change the collecting solvents. The operating conditions can thus be optimized as a function of the compound or compound class involved.

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