CHROMSYMP. 681

PRE-CONCENTRATION OF ORGANIC POLLUTANTS

POTENTIAL INTERFERENCE FROM THE USE OF STYRENE COPOLYMER ADSORBENTS

ADALBERTO BETTI*, SIMONA COPPI and CORRADO BIGHI

Istituto Chimico dell'Università, Cattedra di Chimica Analitica, Via Borsari 46, 44100 Ferrara (Italy)

SUMMARY

The characterization of volatile products released on heating from Porapak Q, Chromosorb 101, 102, and 103 is reported. The structures of these compounds are verified by gas chromatography–mass spectrometry.

The polymers were also extracted with dichloromethane. Thermal and extraction clean-up methods are compared, with the aim of establishing the best conditions for minimizing interference in air-sampling schemes.

INTRODUCTION

In previous papers[1,2] we have pointed out that great care should be used in the choice of the conditioning temperature when styrene copolymers are employed as air samplers. The temperature limit is particularly important if reproducible retention data are to be obtained and if the breakthrough is to be determined accurately. Moreover, thermal treatment at the temperature limit, for at least 3 h, ensures good cleaning of the polymeric surface, reducing the possibility of interference during the thermal desorption process. The temperature limit is the manufacturers' recommended maximum temperature at which the polymers can be heated without decomposition.

In this study, the characterization of volatile products released at the temperature limits from Porapak Q, Chromosorb 101, 102, and 103 is reported. The structures of the organics are verified by gas chromatography–mass spectrometry (GC–MS). The origin of these materials is investigated, with reference to the chromatographic analysis of polymer sample extracts. Thermal and extraction procedures are compared with the aim of establishing the best conditions for minimizing interference in air-sampling schemes.

EXPERIMENTAL

Chromosorb 101, 102 (60–80 mesh), Chromosorb 103, and Porapak Q (80–100 mesh) were supplied by Supelchem (Milan, Italy). The solvents used were of the highest commercially available grade.

A 1.5-g sample of each polymer was heated at the temperature limit for 6 h in a stainless-steel apparatus under ultra-pure nitrogen, flowing at 100 ml/min. The released products were trapped at liquid nitrogen temperature and dissolved in dichloromethane (2 ml). The same amounts of each polymer were extracted for 48-h periods in a Soxhlet apparatus with dichloromethane (40 ml). Solvent volumes were reduced to 2 ml. Both heating and extraction samples were submitted for GC and GC–MS analysis. GC analysis was performed with an OV-1 fused-silica capillary columns (25 m × 0.32 mm I.D.) installed in a Carlo Erba HRGC 5160 Mega Series, equipped with a flame ionization detector. Hydrogen was used as carrier gas, and nitrogen as make-up gas. Samples of 0.5 μl of dichloromethane solutions were injected. All GC–MS analyses were performed on a Finnigan 4500 mass spectrometer. Chromatographic separations were accomplished using an OV-101 3% on Supelcoport (80–100 mesh) glass column (6 ft. × 2 mm I.D.). The temperature conditions were: isothermal 60°C for 6 min, 60–80°C at 8°C/min, 80–140°C at 4°C/min, 140–270°C at 8°C/min. The flow-rate of the helium carrier gas was 20 ml/min and the inlet temperature was 250°C. Sample of 0.5–1 μl were injected. Mass spectrometer operating parameters were the following: scan time, 1.95 s; electron energy, 70 eV; multiplier voltage, 1500 kV; inlet temperature, 250°C. Total ion chromatograms were collected, and individual components spectra were compared with computerized library mass spectra to provide qualitative identifications.

RESULTS AND DISCUSSION

Several different batches of each polymer were investigated in order to obtain representative data. The polymers studied and their physical properties are listed in Table I[3,4].

GC–MS measurements showed that, on heating, the polymers release a variety of materials. Fig. 1 illustrates, as an example, a reconstructed total ion chromatogram of the volatile products evolved from Porapak Q. As confirmed by MS, typical contaminants in this polymer are alkyl derivatives of benzene and styrene.

A more complete listing of the identified compounds for all the polymers is reported in Table II. Contaminants vary according to polymer type, although there is a similarity between Chromosorb 101, 102, and 103. Porapak Q showed a predominance of ethylethenylbenzene isomers and dimethylpropenylbenzene. Chromosorb 102 displayed a predominance of ethenylbenzene and ethylethenylbenzene

TABLE I

PHYSICAL PROPERTIES OF ADSORBENTS

EVB = ethylvinylbenzene; DVB = divinylbenzene; STY = styrene.

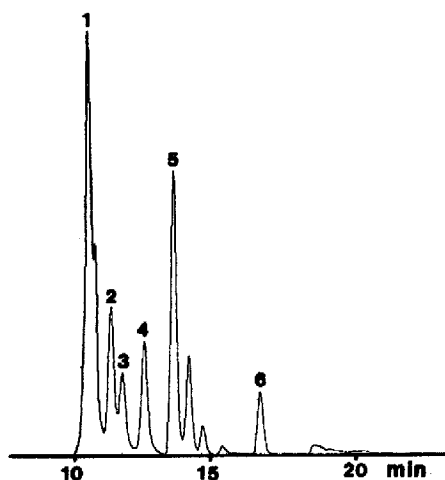| Polymer	Composition	Surface area (m²/g)	Temperature limit (°C)
Porapak Q	EVB–DVB	500–600	250
Chromosorb 101	STY–DVB	<50	275
Chromosorb 102	STY–DVB	300–400	250
Chromosorb 103	Cross-linked polystyrene	15–25	275

Fig. 1. Total ion chromatogram of volatile products evolved from Porapak Q. For GC–MS conditions see Experimental. Peaks: 1 = 1,3- and 1,4-ethylstyrene isomers; 2 = 1,3-divinylbenzene; 3 = 1,4-divinylbenzene; 4 = 3-methylindene; 5 = 1,1-dimethyl-2-propenylbenzene; 6 = 1- or 2-methylnaphthalene.

isomers. Chromosorb 101 and 103 presented chromatograms with more peaks, *i.e.* a higher contaminant level. It must be remembered that the temperature limit of such polymers is greater than that of other polymers. However, Chromosorb 103 showed a predominance of ethenylbenzene, ethylethenylbenzene and dimethylethenylbenzene isomers, whereas Chromosorb 101 evidenced a predominance of ethenylbenzene, ethylethenylbenzene isomers, and ethenylbenzene dimer. It is interesting to note that this polymer also evolved two higher-boiling compounds, *i.e.* dibutylphthalate and dicyclohexylphthalate esters.

TABLE II

CHEMICAL CHARACTERIZATION OF VOLATILE PRODUCTS RELEASED FROM POLYMERS ON HEATING

PQ = Porapak Q; CH101 = Chromosorb 101; CH102 = Chromosorb 102; CH103 = Chromosorb 103.

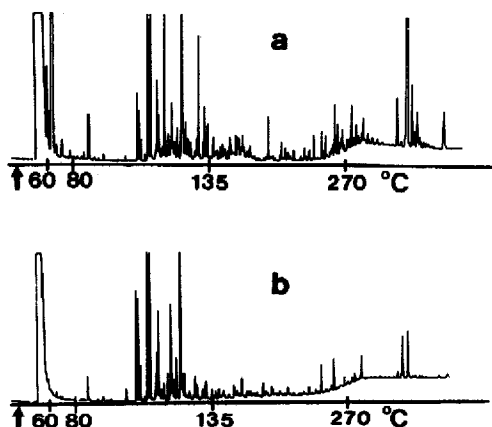| Compound	PQ	CH101	CH102	CH103
1,3-Diethylbenzene (or 1,2- or 1,4-)			★	▲
Triethylbenzene (1,3,5- or 1,2,4-)		■		▲
Ethenylbenzene		■	★	▲
1-Methylethenylbenzene		■		
Ethenylethylbenzene (1,3- and 1,4-isomers)	●	■	★	▲
Dimethylethenylbenzene (1,2,4- or 1,3,4-)			★	▲
Diethenylbenzene (1,3- and 1,4-)	●			
1,1-Dimethyl-2-propenylbenzene	●			
3-Methylindene	●	■		
Naphthalene		■		▲
Methylnaphthalene (1- or 2-)	●	■		
Ethenylbenzene dimer		■		
Dibutylphthalate		■		
Dicyclohexylphthalate		■		

Fig. 2. Glass capillary chromatograms of extractable organics in (a) Chromosorb 101, (b) Chromosorb 102. For chromatographic conditions see Experimental. Attenuation, ×32.

Long-chain esters are widely used as plasticizers in polymer manufacture[5]; mass spectra of these compounds displayed a strong characteristic peak at mass 149.

A weak peak, which can be attributed to dibutylphthalate, appear for Chromosorb 103 after a heating period longer than 6 h. Therefore, such a polymer was further heated. GC analysis showed that phthalic esters are completely released within 12 h of heating. In fact, in a previous paper, it was pointed out that Chromosorb 103 released only a few products after 48 h[6]. Porapak Q and Chromosorb 102 did not show phthalic esters under any heating conditions.

The quantitation of volatile (or extracted) products was not performed, because the levels of organics vary from batch to batch. Furthermore, the aim of this work is to provide a satisfactory clean-up procedure suitable for every polymer batch.

The residual organics released from polymers may be derived from the manufacturing process. To investigate this point, extraction with dichloromethane was
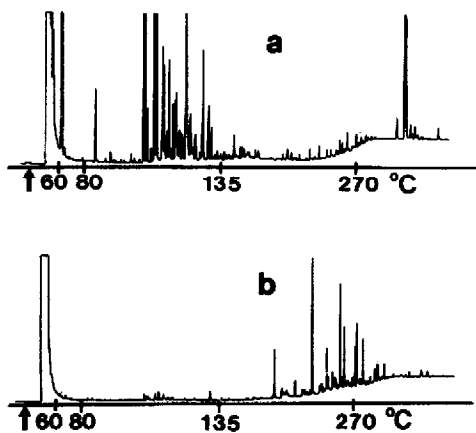

Fig. 3. Glass capillary chromatograms of extractable organics in (a) Chromosorb 103, (b) Porapak Q. For chromatographic conditions see Experimental. Attenuation, ×32.

performed. Hunt and Pangaro[7] characterized organic residues in some XAD resins by an extraction method. It must be remembered that extraction with solvents is widely used as an alternative clean-up procedure[8].

Aliphatic hydrocarbons and their halogen derivatives are indeed good solvents for monomers but not for polymers.

GC capillary analysis of extractable organics is reported in Figs. 2 and 3. Extractions were quantitative after 48 h. In fact, the chromatograms of the polymers already extracted for this period did not show any peaks. Compounds identified by GC–MS carried out on extraction samples are listed in Table III. The majority of these compounds were found in thermal test samples; Chromosorb 101 and 103 extracts showed that the same components and released on heating. Chromosorb 102 extracts had a few more components than the heated sample (*i.e.* naphthalene). Porapak Q extracts are quite different from samples obtained on heating. In fact, the identified compounds are two phthalic esters and some long-chain saturated hydrocarbons. All these products are used as additives in polymer manufacture[5].

Styrene–divinylbenzene copolymers are widely employed as air samplers, although many authors have described disadvantages associated with high blank levels[9]. The manufacturing process leaves a good deal of monomeric material trapped interstitially in the porous structure of the polymer. Such a structure does not seem to be involved in the release of organics during clean-up treatments. In fact, surface area measurements, carried out before and after treatments, gave invariable values[6]. In a previous paper[2] it was pointed out that thermal treatment at the temperature limit for at least 3 h assures good cleaning of the polymeric surface. In fact, the chromatograms of previously treated polymer showed only a few peaks. Since MS confirmations gave similar results, both clean-up procedures seem to be satisfactory.

To confirm this point, similar amounts of each polymer were first extracted and afterwards conditioned at the temperature limit for 3 h. Volatile products released

TABLE III

CHEMICAL CHARACTERIZATION OF EXTRACTABLE ORGANICS

| Compound	PQ	CH101	CH102	CH103
1,3-Diethylbenzene (or 1,2- or 1,4-)			★	▲
Triethylbenzene (1,3,5- or 1,2,4-)		■		▲
Ethenylbenzene		■	★	▲
1-Methylethenylbenzene		■		
Ethenylethylbenzene (1,3- and 1,4-isomers)		■	★	▲
Dimethylethenylbenzene (1,2,4- or 1,3,4-)			★	▲
Diethenylbenzene (1,3- and 1,4-)				
1,1-Dimethyl-2-propenylbenzene				
3-Methylindene		■		
Naphthalene		■	★	▲
Methylnaphthalene (1- or 2-)		■		
Ethenylbenzene dimer		■		
Dibutylphthalate	●	■		
n-Butyl-2-methylpropylphthalate	●			
Dicyclohexylphthalate		■		▲
$n\text{-}C_{14}\text{-}n\text{-}C_{18}$ saturated hydrocarbons	●			
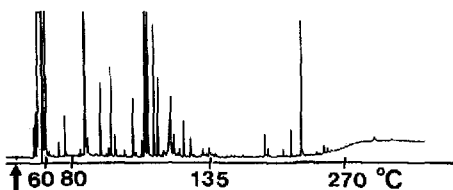
Fig. 4. Glass capillary chromatogram of volatile products evolved from previously extracted Chromosorb 101. For chromatographic conditions see Experimental. Attenuation, × 32.

on heating were trapped, as described in the Experimental section. The chromatogram obtained for Chromosorb 101 (Fig. 4) shows that the polymer still contained appreciable levels of organic residues. Other polymers gave identical results. Therefore, the extraction clean-up procedure is less suitable than the thermal procedure; contaminant materials are largely extractable, but thermal treatment at the temperature limit provides a more rigorous clean-up of polymeric surfaces.

    The appearance of residual artifacts in adsorbents employed in air-sampling schemes can pose a significant problem in the characterization of an environmental sample, expecially during the thermal desorption process. Fig. 5 shows chromatograms obtained during thermal desorption of a Chromosorb 103 tube. In these experiments, the sampling tubes, filled with *ca.* 0.2 g of polymer, were inserted through
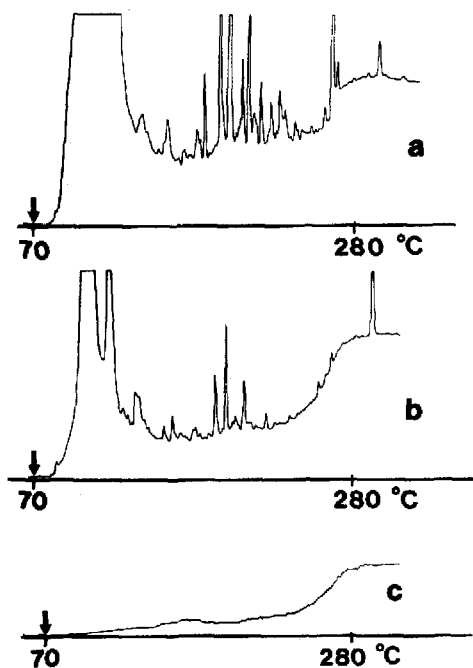

Fig. 5. Blanks of Chromosorb 103 sampling tube obtained during thermal desorption. (a) Polymer pretreated at 200°C for 1 h; (b) polymer extracted with dichloromethane; (c) polymer pretreated at temperature limit for 6 h. Experimental conditions: 3% OV-101, 6 ft. × 2 mm I.D. glass-packed column; temperature, 70–280°C at 8°C/min; detector, 300°C; attenuation, × 32.

a thermostated aluminium block (250°C). It is possible to note that poor blanks are obtained if the polymer is conditioned at a temperature lower than the limit and for a shorter time, as practiced by many workers[10,11]. Poor blanks are also obtained if a polymer is only extracted. Chromosorb 103 provides satisfactory blanks if the sampling tube is conditioned at the temperature limit for almost 6 h. Porapak Q, Chromosorb 101 and 102 gave similar results, but thermal treatment at the temperature limit for at least 3 h is enough.

CONCLUSION

The characterization of volatiles released by heating Porapak Q, Chromosorb 101, 102, and 103 showed that such potential contaminants are manufacturing residues. The majority of them can also be extracted with dichloromethane. Such artifacts can seriously interfere in the subsequent GC analysis if the polymer clean-up procedure is inadequate.

The best conditions for minimizing contamination in air-sampling schemes is to pretreat adsorbents at their proper temperature limit for a suitable period of time, depending on the nature of the polymer.

ACKNOWLEDGEMENT

REFERENCES

1 S. Coppi, A. Betti, G. Blo and C. Bighi, *J. Chromatogr.*, 267 (1983) 91.
2 A. Betti, S. Coppi, G. Blo and C. Bighi, *Ann. Chim. (Rome)*, 74 (1984) 349.
3 *Porapak Porous Polymer Beads GC Column Packing Materials*, Water Assoc., MA, U.S.A.
4 *Chromosorb Century Series Porous Polymer Supports*, Johns-Manville, Denver, CO, U.S.A.
5 M. Baccaredda Boy, *Materie Plastiche ed Elastomeri*, Casa Editrice Ambrosiana, Milan, 1976.
6 S. Coppi and A. Betti, *J. Chromatogr.*, 330 (1985) 55.
7 G. Hunt and N. Pangaro, *Anal. Chem.*, 54 (1982) 369.
8 R. L. Grob, *Modern Practice of Gas Chromatography*, Wiley, New York, 1977.
9 A. J. Núñez, L. F. Gonzáles and J. Janák, *J. Chromatogr.*, 300 (1984) 127.
10 A. Cert and J. Bahima, *J. Chromatogr. Sci.*, 22 (1984) 7.
11 P. Lövkvist and J. A. Jönsson, *J. Chromatogr.*, 286 (1984) 279.