

CHROMSYMP. 1549

## METHOD FOR ANALYSIS OF DILUTE VAPOURS IN FLUE GASES AND WORKING ATMOSPHERES

E. DAVID MORGAN\* and NAIMA BRADLEY

*Department of Chemistry, University of Keele, Keele, Staffordshire (U.K.)*

---

### SUMMARY

Present and forthcoming legislation to control the amount of organic substances emitted in flue gases or present in working atmospheres (*e.g.* laboratories) has required the development of methods for identifying and quantifying parts-per-billion ( $1:10^9$ ) concentrations of a wide range of substances of low and high volatility. A method is described which is applicable to all organic vapours with the exception of very-low-mass compounds. Air or gases to be analysed are passed through an absorption train, containing Tenax GC, the adsorbed organics are desorbed by heating, concentrated into a narrow band, and directly submitted to gas chromatography–mass spectrometry on a Hewlett-Packard 5970B mass selective detector. Substances ranging typically from methyl methacrylate through monoterpenes and plasticizers to nitro- and halobenzenes have been determined as  $\mu\text{g}/\text{m}^3$  in the atmosphere or flue gases.

---

### INTRODUCTION

The increasing use of volatile organic substances in industry and the increasing concern about unnatural substances in the atmosphere have prompted the exploration of methods to measure them and legislation to control their release. In F.R.G., stringent regulations have been made for the concentrations of organic substances permitted in the air of workplaces and in flue emissions<sup>1</sup>. Similar controls will soon be adopted by the European Commission. A directive of the European Economic Community has already been published on combating air pollution, and this applies, among others, to the ceramic industry, for the manufacture of coarse ceramics, refractory, facing and floor bricks, stoneware pipes, and roof tiles. The fine-ceramic industry makes use of a great variety of solvents, adhesives, colour and transfer media, particularly in the application of decoration to pottery and china. When the ceramics are fired in the kiln, these materials are pyrolysed, volatilized, and emitted in the flue gases.

Methods for the analysis of organic substances in the flue gases must therefore be devised. Any method must fulfil at least three requirements. First, it must be as sensitive as possible. Because of the high flow velocities encountered, the volume concentrations may be quite low, and concentration of the contaminants will be necessary. Secondly, the method must be able to detect and quantify a wide range of

substances, in contrast to the specific tests already available (*e.g.*, for vinyl chloride and isocyanates) in other industries. Thirdly, the equipment must be relatively cheap and robust. Sampling equipment may have to be carried to difficultly accessible locations, and many samples may have to be taken because of varying work conditions, raw materials, and types of kiln.

A method is described here which can fulfil these requirements. The organic substances are concentrated by adsorption of flue gases on a polymeric adsorbent, which is then taken to the laboratory. The volatiles are determined by desorbing them directly into a linked gas chromatograph-mass spectrometer.

#### MATERIALS AND METHODS

Glass tubes (400 mm  $\times$  4 mm I.D.) were packed at one end with a column of Tenax GC (130 mm long, 0.35 g, 35-60 mesh) (Enka, Arnhem, The Netherlands), held in place with silanized glass-wool plugs. The packed end of the adsorption tube was connected to a short length of glass tube, containing a platinum resistance thermometer connected to a digital read-out. This tube was connected to a battery-driven, portable diaphragm pump (Model 224-43XR; SKC, Wimborne, U.K.), capable of drawing air through the adsorbent at up to 600 ml/min. This was, in turn, connected through a drying tube to a Singer total flow-meter (International Gas Apparatus, Camberley, U.K.).

For sampling, the empty end of the adsorption tube was inserted through a hole in the flue so that the open end was near the centre of the flue but the Tenax column remained outside the flue and its insulation, if necessary by using an empty extension glass tube. The pump was switched on, and the time, total volume and temperature were recorded. A 10- or 15-l volume of gas was sampled in this way. The adsorption tubes were capped for transport to the laboratory.

The organic vapours were desorbed thermally by placing the adsorption tube inside an electrically heated tubular oven, with a controllable range of 25°C to 350°C. The adsorption tube was heated to 250°C for 20 min while a stream of helium gas (15 ml/min) was passed through it. The outlet was connected to a glass-lined steel tube (SGE, Milton Keynes, U.K.), bent to form a U-tube and cooled in that portion by immersion in liquid nitrogen in a Dewar flask. From the U-tube the glass-lined metal tube ran through a hole in the injection septum, terminating in the heated zone of the injection block. When all the volatiles had been desorbed from the Tenax and collected in the U-tube, the glass-lined metal tube was flash-heated (less than 10 s) to 250°C by passing a direct current through the metal covering, and the plug of organic vapours was swept on to the chromatographic column. Before re-use, the adsorbent was conditioned at 250°C for 3-6 h under a flow of nitrogen.

Separation was performed on a fused-silica capillary column (12 m  $\times$  0.2 mm I.D.), coated with HP-1 (cross-linked methyl silicone gum) of 0.33- $\mu$ m film thickness in a 5890 gas chromatograph (Hewlett-Packard, Bracknell, U.K.), directly coupled to a HP Mass-Selective Detector 5970B with a HP 59970 Chem Station data system. The chromatographic separation was conducted at 30°C for 2 min, then programmed to 160°C at 3°C/min. Identification of the compounds was made from their mass spectra with the aid of the spectrum library. It was checked by injecting known amounts of authentic specimens and correlating retention time and mass spectrum.

Breakthrough volumes ( $V_R$ ) were measured in two ways, by connecting a trap directly to a flame detector<sup>2,3</sup> or by using two traps in tandem<sup>2,4</sup>. Using the flame detector method, which was found more convenient, nitrogen was passed through columns of Tenax of the same dimensions as the adsorbent beds at flow-rates between 150 ml/min and 200 ml/min and temperatures from 150°C to 70°C. Retention volumes were calculated as described by Poole and Schuette<sup>5</sup>.

## RESULTS AND DISCUSSION

### *Adsorption*

Tenax GC (surface area *ca.* 20 m<sup>2</sup>/g) is a porous polymer, based on 2,6-diphenyl-*p*-phenylene oxide. At the start of this work, Tenax GC was used. Later, a grade specifically for adsorption was introduced, called Tenax TA. A survey of the literature shows it to be the most suitable material for adsorption of organic vapours. Its advantages are that it does not absorb water, it is stable at high temperatures (350°C), substances can be eluted from it readily by heating, and it is relatively unselective for compound types. Its one important limitation is that it does not retain very small molecules, so that the method described automatically excludes the collection of methanol, formaldehyde, acetic acid, acetaldehyde, etc. In addition, these substances give very poor response to a flame-ionization detector, and require special methods. We have described two very sensitive methods for determining lower-mass carbonyl compounds<sup>6,7</sup>. The substances released in fine-ceramic firing are of higher molecular mass, and Tenax is a suitable adsorbent.

A reversible adsorbent, such as Tenax, acts like a chromatographic column when gas is passed through it. It is therefore necessary to be sure that the substances are completely retained during the sampling period. A safe sampling volume or breakthrough volume can be defined as the volume of air containing a particular organic contaminant that can be sampled without a significant amount of contaminants being lost by elution from the adsorbent. Some authors draw a distinction between retention volume (which is slightly greater) and breakthrough volume or safe sampling volume<sup>8</sup>. Values for a number of simple compounds have been recorded<sup>8-10</sup>. Because these values may vary with the size and shape of the adsorbent bed, flow-rate, concentration, etc., we have carried out some experiments to check the breakthrough values of the least-retained compounds met in our analyses, under conditions similar to those we were using. The flow-rates used in determining  $V_R$  were only half of those used in actual sampling, but it has been shown<sup>9</sup> for Tenax that  $V_R$  values are essentially independent of flow-rate between 100 ml/min and 1000 ml/min.

Plots of  $\log V_R$  against  $1/T$  K ( $T$  = temperature), measured at elevated temperatures, gave straight lines, from which values at ambient temperatures could be extrapolated. Some representative values are given in Table I for three substances frequently encountered in sampling. It can be seen that breakthrough volumes are highly dependent upon temperature, and that terpenes have very low breakthrough volumes<sup>11</sup>, but these are strongly dependent upon concentration. Riba *et al.*<sup>11</sup> showed that they increase strongly for concentrations less than 5 ppm (28 mg/m<sup>3</sup>) and, a breakthrough volume of 12 l/g is recorded for  $\alpha$ - and  $\beta$ -pinene at 100 ppb<sup>12</sup> or 0.55 mg/m<sup>3</sup>.

The temperature of the adsorbent during sampling is clearly critical. In practice,

TABLE I

## BREAKTHROUGH VOLUMES OF SOME REPRESENTATIVE LOW-RETENTION SUBSTANCES IN THE FLUE GASES FROM CERAMIC KILNS

Column, 0.35 g Tenax.

Substance	$V_R$ (l)		
	20°C	35°C	250°C
Methyl methacrylate	42	12.6	$2 \cdot 10^{-4}$
Butyl methacrylate	1400	300	$1 \cdot 10^{-3}$
$\alpha$ -Pinene	1.3 <sup>a</sup>	0.12	<sup>b</sup>

<sup>a</sup> At 20 ppm (from ref. 11).<sup>b</sup> Unretained.

although flue gases are considerably diluted with ambient air drawn into the flue by fans, the temperature in the flue can be as high as 300°C. Preliminary experiments showed that the concentration of pollutants was not critical. The values found were 10–100 times the concentration of organic pollutants in air (Table II)<sup>13</sup>. There was therefore no fear of overloading the adsorbent, sampling could be done in a reasonable time, and to seek much greater sensitivity would have been pointless. Flow-rates allow considerable latitude and were chosen as a compromise between short sampling time and maintaining a low temperature.

Typical total-ion chromatograms are shown in Figs. 1 and 2. The levels of these substances are well below the limits in present legislation and are not a serious contribution to atmospheric organic contaminants. Typical values obtained for a number of samples taken at different times from a kiln, where transfer-decorated pottery was fired, are given in Table III. Further work is in progress on other systems, where flue gases and combustion gases are mixed and can contain soot and large amounts of water vapour.

Legislation in Britain will soon be extended to control of substances hazardous to health in laboratory atmospheres, and it will make provision for controls necessary as the result of the discovery of hitherto unsuspected substances. From our preliminary studies, this method is highly suitable for monitoring of research laboratories where low levels of toxic and constantly varying organic contaminants may be encountered.

TABLE II

## RANGE OF SOME MAJOR SUBSTANCES DETERMINED IN THE FLUE GASES OF DECORATIVE CERAMIC KILNS

Concentration and total amount vented to the atmosphere are given. Atmospheric values are reduced to a temperature of 0°C.

Compound	Concn. ( $\mu\text{g}/\text{m}^3$ )	Total amount (mg/h)
Methyl methacrylate	57–1.6	164–10
Butyl methacrylate	151–1.2	450–5

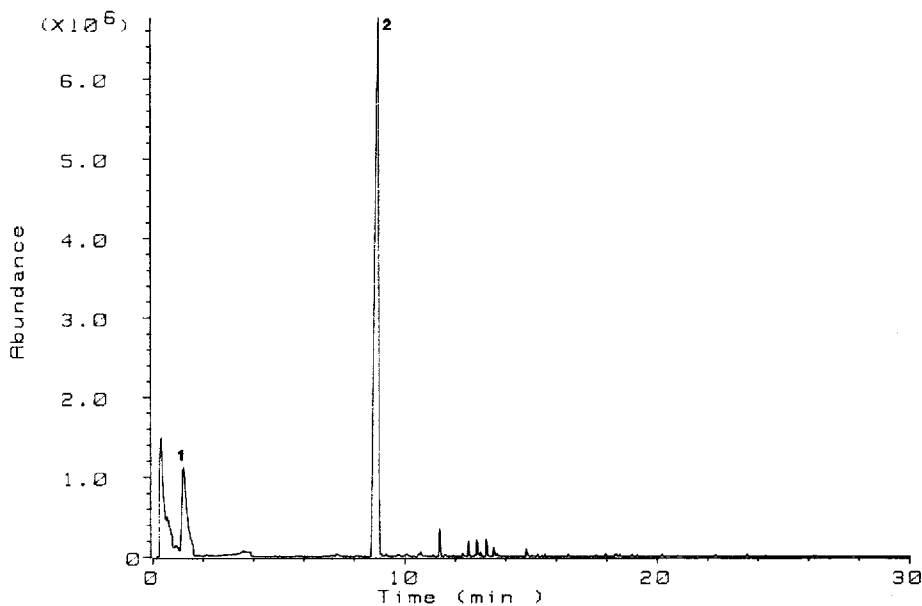


Fig. 1. Total-ion chromatogram obtained from flue gases of kiln firing ceramics decorated with transfers. Peaks: 1 = methyl methacrylate; 2 = butyl methacrylate. Broadening of the methyl methacrylate peak is caused by the "vacuum effect" of having a capillary column directly coupled to a mass spectrometer<sup>14</sup>.

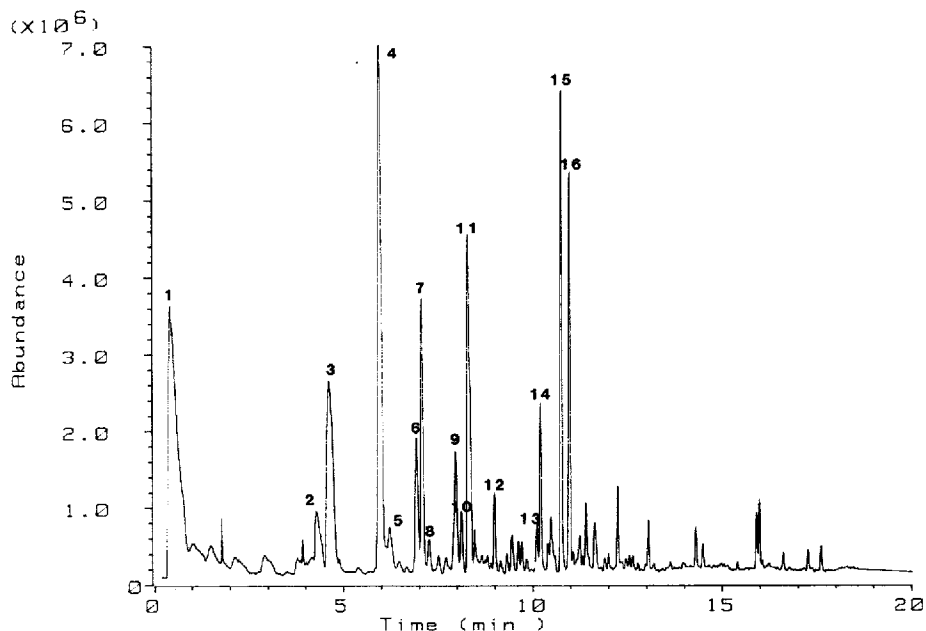


Fig. 2. Total-ion chromatogram obtained from flue gases of kiln firing hand-decorated ceramics. Identified substances: 1 =  $\text{CO}_2$ ; 2 = cyclohexanone; 3 = 2-methylcyclopentanol; 4 =  $\alpha$ -pinene; 5 = camphene; 6 =  $\beta$ -pinene; 7 = butyl methacrylate; 8 = toluene; 9 = dichlorobenzene; 10 = *p*-cymene; 11 = cineole (eucalyptol) and limonene; 12 = *o*-cymene and nitrobenzene; 13 = trimethylcyclohexanone; 14 = carene; 15 = camphor; 16 = nitrotoluene. Early peaks are broadened by the "vacuum effect"<sup>14</sup>.

TABLE III

RANGE OF VALUES FOUND AT DIFFERENT SAMPLE VOLUMES FOR THE MAJOR ORGANIC CONTAMINANTS IN A SINGLE KILN

Results are given in concentration ( $\mu\text{g}/\text{m}^3$ ) and total material vented to the atmosphere ( $\text{mg}/\text{h}$  at  $0^\circ\text{C}$ ). Substances identified as major organic contaminants in Briesco kiln vent.

	Sample size (l) at room temp.	Sampling temperature ( $^\circ\text{C}$ )	Methyl methacrylate		Butyl methacrylate	
			$\mu\text{g}/\text{m}^3$	$\text{mg}/\text{h}$	$\mu\text{g}/\text{m}^3$	$\text{mg}/\text{h}$
Sample 1	5	26	12.3	37	58.1	170
Sample 2	5	26	6.1	17	23.2	70
Sample 3	5	26	32.7	92	151	430
Sample 4	10	25	45.0	130	116	337
Sample 5	10	27	20.5	55	110	322
Sample 6	10	25	20.5	58	98.7	285
Sample 7	15	25	57.2	164	104	308
Sample 8	15	25	32.7	92	69.7	205
Sample 9	20	26	20.5	55	134	386
Sample 10	20	26	16.3	49	63.9	178

#### ACKNOWLEDGEMENTS

We thank the Trustees of the SAC Trust fund of the Royal Society of Chemistry for the award of a studentship, the Royal Society and the Science and Engineering Research Council for grants for the purchase of equipment. We are very grateful to W. H. Holmes, D. L. Salt, and E. Davies of British Ceramic Research Ltd., Stoke-on-Trent, U.K., for valuable help and collaboration.

#### REFERENCES

- 1 *Technische Anleitung zur Reinhaltung der Luft*, Bundesministerium des Innern, Bonn, Aug. 28, 1974, pp. 16–20, Modification, 1986, pp. 12 and 13.
- 2 E. D. Pellizzari, J. E. Bunch, R. E. Berkeley and J. McRae, *Anal. Lett.*, 9 (1976) 45.
- 3 G. I. Senum, *Environ. Sci. Technol.*, 15 (1981) 1073.
- 4 G. Holzer, H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield and H. M. Liebich, *J. Chromatogr.*, 142 (1977) 755.
- 5 C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984, p. 2.
- 6 D. G. Ollett, A. B. Attygalle and E. D. Morgan, *J. Chromatogr.*, 367 (1986) 207.
- 7 D. G. Ollett and E. D. Morgan, *Microchem. J.*, 35 (1987) 296.
- 8 R. H. Brown and C. J. Purnell, *J. Chromatogr.*, 178 (1979) 79.
- 9 R. F. Gallant, J. W. King, P. L. Levins and J. F. Piecewicz, *EPA-600/7-78-054*, U.S. Environment Protection Agency, Springfield, MA, March, 1978.
- 10 C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984, p. 478.
- 11 M. L. Riba, E. Randrianalimanana, J. Mathieu, L. Torres and J. Namiesnik, *Int. J. Environ. Anal. Chem.*, 19 (1985) 133.
- 12 Y. Yokouchi, T. Fujii, Y. Ambe and K. Fuwa, *J. Chromatogr.*, 209 (1981) 293.
- 13 C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984, p. 480.
- 14 K. Peltonen, U. M. Lakkisto and C. Rosenberg, *LC · GC Int., Mag. Liq. Gas Chromatogr.*, 1 (1988) 48; *LC · GC, Mag. Liq. Gas Chromatogr.*, 6 (1988) 524.