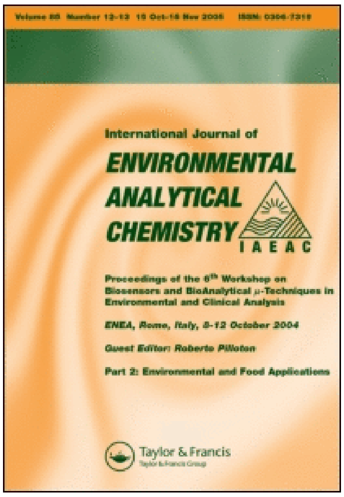

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Atmospheric Analysis Using a Micro Carbon Sampler

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A sampling device for atmospheric analysis is described, and its use compared with the use of evacuated flasks. Carbon adsorbent is held on a Curie point pyrolysis wire, and desorption prior to gas chromatographic analysis is brought about by heating the wire to its Curie point. The analysis of factory atmospheres is described and the results compared with identical samples taken in evacuated flasks. Organic compounds present in concentrations from 1 to 100 ppm can be analysed using this device, making it applicable to the monitoring of atmospheres for compounds at and below their threshold limit values.

KEY WORDS: Atmospheric analysis, carbon adsorption.

INTRODUCTION

The analysis of atmospheres, especially in the workplace, for vapours of organic compounds has become increasingly important with the realisation of the adverse effects of many compounds. Many systems of varying degrees of sophistication have been devised for the sampling and analysis of organic compounds present in air samples at the parts per million (ppm) level and below.[1–7] Frequently the concentrations of compounds are too low to be measured directly and so the sampling procedure involves a concentration step. In many cases this involves adsorption onto the surface of an adsorbent and subsequent desorption by heat or solvent. Active carbon has been used by many workers[1,2,4–6] as the adsorbent.

Recently a simple sampling device using active carbon has been described.[8,9] The technique assumes that gas chromatography will be adopted as the means of analysis since it involves the use of a Curie point pyrolysis gas chromatography unit. In this method a few grains of active carbon are held on a wire, and this is used as the sampler. After exposure to the atmosphere the sampler is transferred to the Curie point pyrolysis unit, and desorption takes place as a result of the wire being heated to its Curie point by means of a Rf supply. The previous work showed that in many cases desorption of the adsorbate takes place quantitatively and without pyrolysis of the sample.

The work described in this paper shows the application of such a device to the sampling of atmospheric samples and compares the results with those obtained using an evacuated flask for sampling.

EXPERIMENTAL AND RESULTS

The sampler was a Curie point pyrolysis wire with a loop formed at one end into which a few grains of active carbon were inserted. Wires with a range of Curie points from 358 to 770°C are available commercially. For this work wires with a Curie point of 480°C were used. Desorption of the adsorbate from the active carbon was achieved by heating the sampler in a Becker Packard Model 891 Pyrolysis Unit. The pyrolyser was connected directly to the top of a gas chromatographic column enabling direct injection of the adsorbate onto the column. The gas chromatograph used was a Perkin Elmer Model F11 fitted with a flame ionisation detector (F.I.D.) and an electron capture detector (E.C.D.).

For comparison sampling was also carried out with evacuated glass flasks. Each glass flask, of 1 litre capacity, was fitted with a Teflon "Rotaflo" screw tap through which samples could be taken for analysis.

Sampling using the active carbon sampler was carried out in one of two ways. The sampler could be exposed to the atmosphere for a specific period of time, normally a few tens of seconds. Both before and after sampling the sampler was stored in a narrow glass tube sealed at both ends with Teflon caps. Alternatively the sampler could be left in the glass tube, the Teflon caps removed, and the air sample drawn through the tube and over the sampler by means of a suitable pump. A Factory Inspectorate Pump has been used for this purpose. The use of the pump produced a more controlled adsorption process and this was generally preferred. Where the concentration of organic compounds was below 1–10 ppm the use of the pump was essential to allow concentration to take place.

Calibration plots for each compound analysed were produced by preparing standard atmospheres of known concentration and sampling these in the manner described. Standard atmospheres were made by injecting a measured volume of the test compound into a flask of suitable capacity through a serum cap. A magnetic stirrer was used to ensure a homogeneous atmosphere. Samples to be analysed were withdrawn from the flask through the serum cap.

Samples were taken in a factory, where a number of solvents were in use. The predominant solvents were *m*-xylene and butanol, although several others were present. Fig. 1 is a chromatogram of an air sample taken by means of the carbon sampler. For the analysis a 2 m × $\frac{1}{4}$ in. outer diameter glass column was packed with 5% Carbowax 20M on acid washed 80/100 mesh Chromosorb W. An oven temperature of 60°C was used with a nitrogen carrier gas flowrate of 20 ml $\cdot$ min^{-1}.

The compounds marked on the chromatogram were identified by direct injection of standards at the same analytical conditions. Calibration plots were made for toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and *n*-butanol. Straight lines were obtained by direct syringe injection of the air sample and also after sampling using the Curie point sampling system; regression coefficients in the 1–100 ppm range typically were 0.95–0.98. Desorption was carried out for 5 sec at 480°C, and the desorbed compounds passed directly onto the column. Table I shows the results obtained using the two techniques.

A further series of tests was carried out on a factory atmosphere where acrylonitrile was suspected of being present. For this analysis the gas chromatographic conditions were the same as for the previous analysis except that the oven temperature was 70°C. Table II shows the results obtained using the carbon sampler and evacuated flasks for the factory atmosphere and for standard atmospheres produced in the laboratory.

DISCUSSION

This work demonstrates that the carbon sampler combined with Curie point desorption is a valuable alternative to the other techniques available for air pollution sampling. Together with gas chromatographic analysis it provides a powerful tool in the analysis of polluted atmospheres. The principle advantages of the method are its speed and simplicity. Many gas chromatography laboratories already possess the equipment demanded, and no modification is necessary. With some experience the samplers can be made quickly and easily. They have proved to be remarkably robust and can be reused many times.

In the analyses described here the pollutants determined were in concentrations between 1 and 100 ppm. Compared with the nominal concentrations of standard atmospheres and the results obtained by different methods the results produced were slightly low, but nevertheless acceptable. The two processes involved, adsorption and desorption from

TABLE I

Comparison of results obtained using the carbon sampler and an evacuated flask

Position	Concentration measured in ppm											
	Toluene		Ethylbenzene		*o*-Xylene		*m*-Xylene		*p*-Xylene		*n*-Butanol	
	C.S.	Flask	C.S.	Flask	C.S.	Flask	C.S.	Flask	C.S.	Flask	C.S.	Flask
1	0.8	N.D.	0.5	N.D.	0.5	N.D.	1.2	1.1	0.4	N.D.	0.6	N.D.
2	1.7	1.5	13.9	14.7	12.5	12.2	36.0	37.9	15.0	15.1	22.6	23.8
3	0.1	N.D.	0.2	N.D.	0.1	N.D.	0.7	N.D.	0.1	N.D.	0.5	N.D.
4	1.1	N.D.	6.8	6.8	9.4	9.8	25.0	26.2	10.4	10.7	12.5	11.9
5	0.2	N.D.	0.6	N.D.	0.2	N.D.	1.1	1.0	0.2	N.D.	0.6	1.0
6	0.7	N.D.	0.6	N.D.	0.8	1.0	15.9	15.5	11.3	11.5	7.8	6.9

N.D. not detected.

TABLE II

Comparison of Acrylonitrile concentration measured using the carbon sampler and an evacuated flask

Sample	Nominal concentration	Found by sampler[a]	Found by flask*
1	1.5	1.3	N.D.
2	10.0	9.7	9.9
3	21.5	20.8	21.2
4	52.0	50.0	51.6
5	97.5	94.0	96.8
6	—	2.5	2.8
7	—	12.4	12.5
8	—	15.0	15.2

[a]Each figure is the mean of five determinations.
N.D., not detected.

the carbon surface, have been studied,[9] and the adsorption process in a dynamic sampling process has proved to be the less efficient, although over 90% adsorption is possible. The limiting factor in adsorption is the mass of carbon which can be incorporated in the sampler. Since the sampler is relatively small, and because the heating capacity of the device is limited the mass of carbon is small. However within the range of concentrations examined here the performance was excellent.

The small mass of carbon can be a disadvantage in the analysis of atmospheres where the pollutant concentration is below 1 ppm since in such cases the volume of gas necessarily sampled may be sufficient to cause break through of some compounds. However, the mass of compound required for detection is a function of the detector system and in some instances the sampler may be useful in the sub-ppm range.

Problems may also arise in the analysis of atmospheres of high concentration. The mass of adsorbate which can be held on the adsorbent surface as a monolayer is limited and compounds subsequently adsorbed may be less strongly held. Such overloading of the sampler is apparent when the sampler is placed in the pyrolysis unit. Before any controlled desorption is brought about slow desorption begins under the influence of the carrier gas stream and grotesquely shaped peaks are observed on the chromatogram. In suitable cases the problems associated with overloading can be eliminated by reducing the sampling period. However, where the pollutant concentration is very high it may not be possible to sufficiently reduce the sampling time to give a manageable degree of adsorption, and in such situations this sampler cannot be recommended.

The range wherein this method functions most effectively is fortunately that of greatest interest. Thus the threshold limit values (TLV) of a great number of compounds is between 1 and 100 ppm and this method should be of benefit in the monitoring of atmospheres for these compounds. It was in this context that the device was used in this work, and quite clearly it is possible to discriminate between areas where the particular compounds are above and below the TLV. Since the method is essentially fast a series of samples can be taken throughout, for example, a process and the fluctuations in concentration measured as a function of time. When the system was operated within the recommended concentration range the chromatograms obtained compared favourably with similar ones obtained by the direct injection of gas samples. Fig. 1 shows few traces of tailing, and is virtually identical to that obtained by direct injection. Any deterioration of chromatographic performance is as a result of the slight increase of dead volume in the system. For analysis on packed columns this seems not to be important and the results compare favourably with those achieved by other methods.

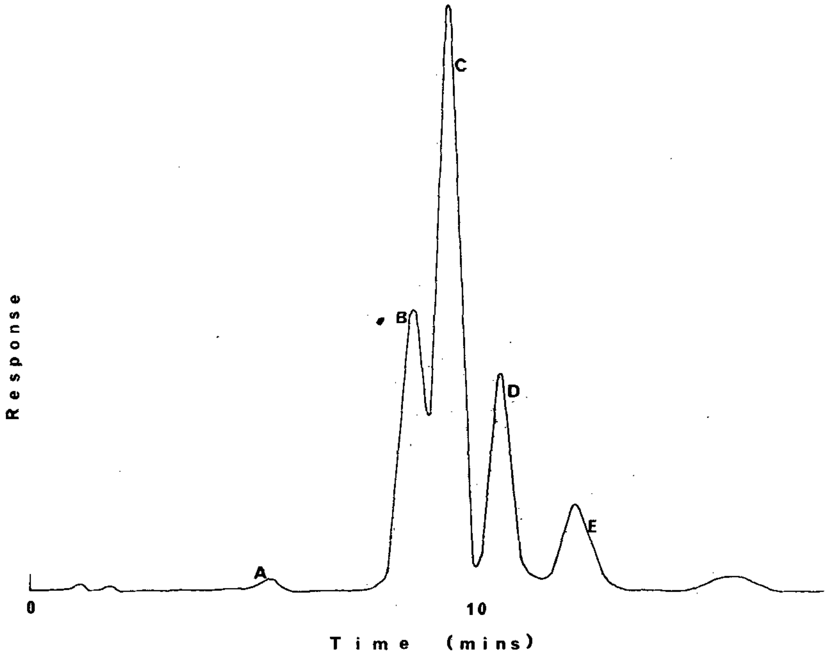

FIGURE 1 Chromatogram of factory air sample taken using the carbon sampler. A, toluene; B, ethylbenzene; C, *m*-xylene; D, *n*-butanol; E, *o*-xylene.

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