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Atmospheric Sampling for Public Health Investigations Using Adsorption Tubes with Quantitative G.C. or G.C./M.S. Analysis

B. I. BROOKES, S. M. JICKELLS AND R. S. NICOLSON

Department of the Regional Chemist, Strathclyde Regional Council, 8 Elliot Place, Clydeway, Glasgow

Air sampling techniques using Porapak Q and Tenax G.C. adsorption tubes are described for the collection of a wide range of organic pollutants. The sample is transferred by thermal desorption to a GC column followed by temperature programmed G.C. or G.C./M.S. analysis. The collection and sample recovery systems can be constructed without great expense or special expertise.

A method is reported for the measurement of retention volumes, and the estimation of collection efficiencies of organic compounds on the sample tubes. Such data are reported for ethanol, acetone, benzene, pyridine, toluene, styrene, furfural, naphthalene, nicotine and phenanthrene.

A method for the quantitative interpretation of routine analyses is illustrated by reference to some examples of the authors' work.

Many methods have been developed for the sampling and G.C. analysis of trace organic pollutants in air, but most have serious disadvantages if they are to be put to routine use in a non-specialised laboratory.

Enclosure methods are the simplest, the air being drawn into a glass or plastic vessel so that it can be transported to the laboratory where portions can be injected into the G.C. using a gas-tight syringe.[1–3] However, these methods lack sensitivity and there are difficulties in avoiding losses to, and contamination from, the walls of the containing vessel. In a review article, Robinson *et al.*[4] have suggested that terylene and nylon are the only suitable materials for plastic sample vessels. Perhaps P.T.F.E. could also be added to this list, but it is very expensive.

Cryogenic trapping techniques using dry ice or liquid nitrogen have been reported. The difficulties of accommodating the large amounts of water and carbon dioxide, which condense along with the pollutants, can be overcome[5–9] but these methods require rather bulky sampling equipment, trained personnel to operate it, and a regular supply of the coolant.

Adsorption techniques, in which a tube containing carbon,[9–12] or a polymeric adsorbent[5,13–18] is used to take up the pollutants as the air is drawn through it, have found the most widespread use, but these also have their defects. Pellizzari *et al.*[13] have reported poor collection efficiency on graphitised carbon and

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there is a danger of catalytic decomposition with those techniques where thermal desorption is used to recover the sample from a carbon adsorbent. Perhaps the most elegant techniques are those using carbon with solvent recovery,[9,10] and those using polymeric adsorbent with recovery by thermal desorption. A certain amount of expertise is required with these, particularly in the use of carbon. The thermal desorption techniques mostly require facilities and services that are rarely available outside specialised laboratories, and modifications often have to be made to the G.C. which are a hindrance to the more routine usage of the equipment.

Three papers have recently appeared describing sampling methods with polymeric adsorbents which do not have these disadvantages. The simplest of these is that of Williams and Umstead.[19] The sample is collected by drawing the air under investigation through the G.C. column—the pollutants collect at the head of the column, and can be analysed by temperature programmed chromatography. This method has the advantage over most others that there is no need to transfer the sample from the sample tube to the column, since they are one and the same. However, the sampling rate is slow and the sample tube is bulky and expensive. In the method of Sickels and Stafford[5] the air pollutants are taken up on a short adsorption tube which is subsequently connected to the injection port of the chromatograph. A commercially available thermal flasher is used to vaporise the sample and then it is swept on the column. Mieure and Dietrich[16] describe two methods. In the first, the adsorption tube, containing the sample, is attached to the injection port of the G.C. column and the sample is discharged on to the column by lowering a hot, cylindrical oven around it. In their second method, the tube is attached to a modified column inside the G.C. oven so that it sits between the injection port and the column. Analysis is carried out by temperature programmed chromatography. There is difficulty with this last method in making a satisfactory tube to column coupling which will repeatedly survive the pressures and high temperatures employed on the chromatograph.

We have explored these methods and several modifications. We report here the three methods which we have found to be most satisfactory. All three are similar in essence to the first method of Mieure and Dietrich. They each have advantages and disadvantages depending on the type of work to be carried out.

In addition, we report a method for the quantitative interpretation of the results. Very little attention has been paid to this aspect of the work in the literature. Of those reviewed above, only the paper by Butler and Burke[15] gives serious consideration to the factors involved. They take a theoretical approach to the problem and demonstrate the method for determining the precise sample volume which would permit a minimum 99 per cent. sampling efficiency for a given compound on a given adsorbent. However, their work covers only a small number of compounds and needs to be extended if it is to be of general applicability. Our approach is based on a few simple assumptions which produce less precise results than those of Butler and Burke, but nevertheless permit sample volumes to be calculated for the sampling of a wide range of compounds with a high collection efficiency.

Experimental

APPARATUS

Sample Tubes

The sample tubes are prepared as illustrated in Figure 1 from Pyrex glass tubing packed with 0·5 g of 100–120 mesh, Porapak Q, or 0·25 g of 60–80 mesh, Tenax G.C. (both from Chromatography Services Limited, Merseyside).

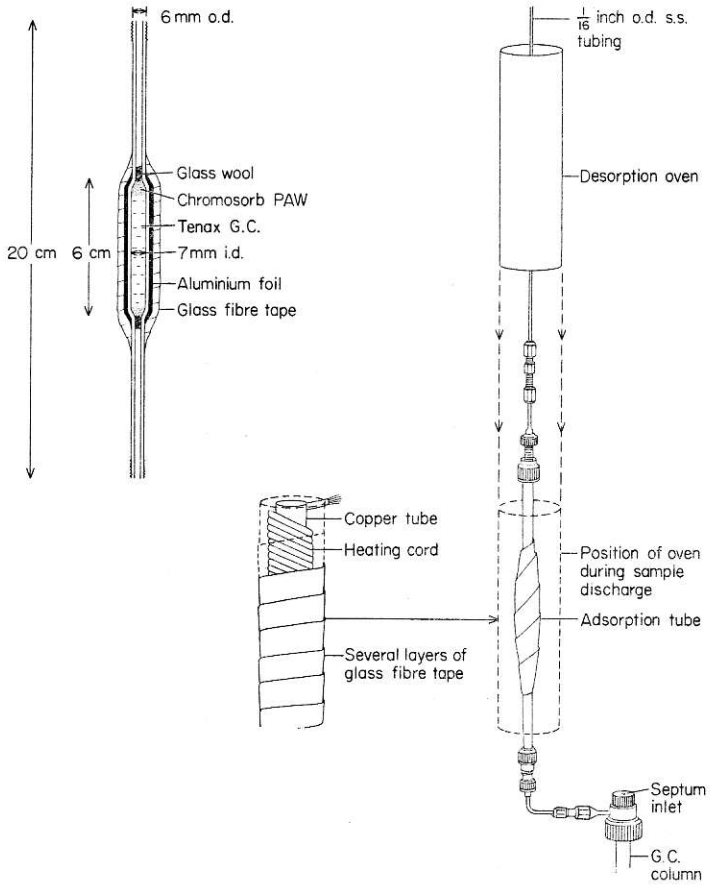

Fig. 1. The sample tube and its attachment to the G.C. in Method (1).

The two layers of Chromosorb PAW act as inert buffers to ensure that all of the Tenax G.C. remains in the centre of the tube. The resistance to air flow of each tube is fixed during its construction by adjusting the compaction of the glass wool plugs, so that the flow rate during sampling is 7 ml/sec. or less. The diameter of the adsorbent bed, 7 mm, is critical since it affects the efficiency of the thermal desorption process.

When not in use the tubes are sealed with $\frac{1}{4}$ inch G.C. column caps and stored in 9 inch $\times$ 1 inch boiling tubes fitted with rubber bungs.

Sampling Equipment

A Dymax Mk II A air sampling pump (Gallenkamp) fitted with a bubble flow meter on the pump outlet and $\frac{1}{4}$ inch i.d. PVC tube on the pump inlet.

A Draeger hand pump.

Desorption Oven

See Figure 1. A copper tube, 2 cm diameter and 15 cm long, wound with heating cord and glass fibre thermal insulation tape (the last two from Gallenkamp) and controlled by a V8HM variable transformer (Zenith Electric Co. Limited, Milton Keynes).

Adsorption Tube to G.C. Couplings

Method (1): See Figure 1. Two Pye Unicam, $\frac{1}{4}$ inch, O-ring couplings; one Pye Unicam 1/16 inch union; 1/16 inch o.d. stainless steel tube; 19 cm of 6 mm o.d. Pyrex glass tube with a 1 mm bore.

Method (2): A 1/16 inch o.d. stainless steel, carrier gas supply line connected to the adsorption tube through a $\frac{1}{4}$ inch o.d. O-ring coupling; and the tube to column connection made with a $\frac{1}{4}$ inch stainless steel Swagelok union, fitted with silicone rubber O-rings (the O-rings from Analabs).

Method (3): A Pye Unicam, six port, gas sampling valve is fitted in the G.C. carrier gas supply line between the G.C. needle valve and the septum inlet. The valve has two O-ring couplings arranged to take the adsorption tube in place of its sample loop.

Gas Chromatograph

Oven	Pye Unicam, Series 104 Chromatograph oven.
Columns	A 2 metre $\times$ 2 mm, glass column packed with 60–80 mesh Tenax G.C.; a 2 metre $\times$ 2 mm, glass column packed with 100–120 mesh Chromosorb 101.
Carrier Gas	Medical grade helium, purified by passage through a 13 $\times$ molecular sieve filter; flow rate = 20 ml/min.

Detection System

A V.G. Micromass 16B mass spectrometer interfaced to the G.C. via a V.G. jet separator. Equipped for the fast scanning of a wide mass range, it can produce chromatograms and the associated mass spectra; also equipped with a selective ion monitoring system which is used for work requiring the greatest sensitivity and specificity (V.G. Micromass Limited, Altrincham).

The Eight Peak Index of Mass Spectra (MSDC, Aldermaston) used for the identification of the mass spectra.

Note: The more conventional G.C. detection systems such as FID are also used successfully for this type of work.[4,6,13,16,19]

Clean Air for Blank Analyses

A supply of moist, clean air, i.e. air free from organic contaminants, is obtained by drawing air through a 30–60 mesh, activated charcoal filter, then

through a Dreschel bottle containing distilled water, and finally on to the adsorption tube. The suction can be provided either by the Dymax pump listed above or by a water pump.

Additional Apparatus for Measuring Retention Volumes

Tube measurements: A sample tube packed with a known weight of the adsorbent.

A commercial G.C. exit splitter (or one can be made as described under tube measurements, in which case the following are required to connect it to the G.C.: $\frac{1}{4}$ inch o.d. Teflon tube (Phase Separations Limited), 1/16 inch stainless steel tube, a $\frac{1}{4}$ inch o.d. O-ring coupling, and a Pye Unicam 1/16 inch union).

Column measurements: A 2 mm × 2 metre glass column packed with a known weight of the adsorbent.

SAMPLING

With the Dymax Electrical Pump

Connect the adsorption tube to the pump with the PVC tube and measure the flow rate on the bubble meter. Draw the air to be sampled through the tube for a measured period of time. Check the flow rate at the end of the sampling period, re-seal the tube with the rubber caps and store it in the boiling-tube.

With the 100 ml Draeger Hand Pump

Attach the sample tube to the pump in the same way as for Draeger tubes, and pump the required volume of air.

Caution: Allow at least 5 seconds at the end of each stroke for the passage of the full volume of air (100 ml).

SAMPLE DESORPTION TO THE G.C. COLUMN

Method (1)—Tube to Column Transfer via the Septum Inlet

See Figure 1. This is suitable for both the volatile and the less volatile components of the sample. Connect the tube between the carrier gas supply line and the column. Discharge the sample by lowering the cylindrical oven (preset to 200°C for Porapak Q tubes, or 250°C for Tenax G.C. tubes). After 5 minutes begin the temperature programme. For a sample being analysed for its more volatile components, the sample should be discharged on to the Chromosorb 101 column at room temperature and temperature programmed from 100°C to 235°C at 10°C per min. Discharge other samples on to the Tenax G.C. column and temperature programme from 50°C to 350°C at 10°C per min. The desorption oven should remain in position on the tube for the whole of the analysis period. At the end of the programme standardise the analysis by making injections of one or more standard solutions, e.g. 1 μl of 0·2 per cent. ethyl acetate in methanol on Tenax G.C. at 130°C or on Chromosorb 101 at 200°C. The use of an internal standard is not practicable in this work. Report the preliminary results semi-quantitatively by quoting the chromato-

gram peak heights relative to the external standard as approximate concentrations in the original volume of air. For example:

Compound	Peak height	Height relative to standard	Sample volume, *litre*	Approximate concentration†, *μg/litre*
Compound *X*	x	x/s		$2x/sV$
Compound *Y*	y	y/s		
			V	$2y/sV$
2 μg of standard	s	—		—

† Assuming similar, and linear, detector sensitivity for all compounds.

For quantitative work, calibrate the technique by injecting known amounts of the compounds of interest on to adsorption tubes, drawing the compounds into the tubes with about 1 litre of clean air, and analysing the tubes in the normal way. Draw the calibration graphs by plotting "peak height relative to the external standard" versus "amount injected".

Method (2)—Tube to Column Transfer away from the Oven

This is suitable for both volatile and less volatile compounds. It can be used with any model of G.C. Carry out the transfer as in method (1) but with the column and tube removed from the G.C. and connected to a separate carrier gas supply line. Heat the tube for 30 minutes to discharge the sample completely on to the column, then replace the column in the G.C. oven and analyse as above.

Method (3)—Tube to Column Transfer via a Gas Sampling Valve

This is suitable for the more volatile compounds only. Connect the adsorption tube to the sampling valve in place of the sample valve loop.. Purge the residual air from the tube and switch the tube into the G.C. carrier gas supply line. Carry out the sample transfer and analysis in a similar way to method (1).

BLANK ANALYSIS

To confirm that the adsorption tube was completely purged of its sample during the analysis, carry out a blank by disconnecting the tube, drawing 5 litres or more of clean air through it, and repeating the analysis. The tube is usually found to be completely purged of its sample, in which case it is ready for its next assignment. Keep a record of the blank analysis with the tube as evidence that it is clean.

MEASUREMENTS OF RETENTION VOLUMES

Tube Measurements

Apply a high carrier gas pressure to the G.C. (50 p.s.i. or more) and control the flow rate with the G.C. needle valve. This will ensure a constant carrier gas flow rate during the measurements. Fit the tube into the G.C. oven at the septum inlet. Connect to the splitter and to the detector. (A splitter can be

made by drawing out one arm of a $\frac{1}{4}$ inch o.d. glass, Y-tube into a jet. Connect one of the wider arms to the sample tube with $\frac{1}{4}$ inch o.d. Teflon tubing and connect the other to the detector with a $\frac{1}{4}$ inch o.d. Pye Unicam, O-ring coupling and 1/16 inch stainless steel tube. Shorten the length of the splitter jet until the flow of carrier gas to the detector, measured by a bubble flow meter, is about 1/10 that through the jet.) Measure the flow rates at the splitter jet and the detector ambient temperature and adjust the needle valve to give a total ambient flow which is similar to that which is used when sampling air.

Inject 2 ml of the headspace vapour from a reagent bottle containing the compound of interest and measure the retention volumes with respect to the peak maximum, over a range of temperatures. Note that the peaks resulting from these injections are much broader than the corresponding peaks obtained on a G.C. column (see Figure 2).

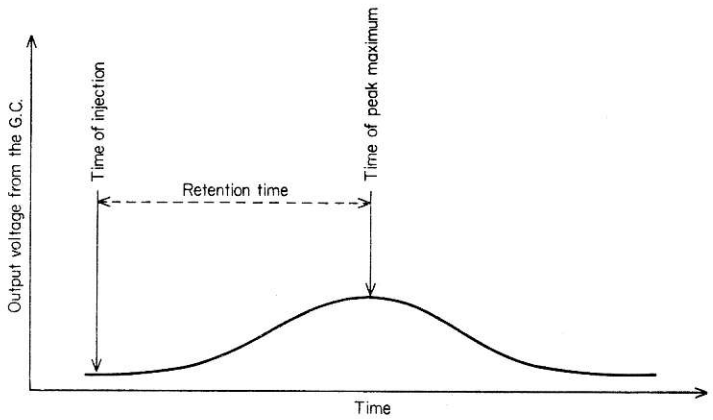

Fig. 2. The measurement of retention volumes.

The retention volumes are determined from the expression:

Retention volume = retention time × real flow rate.

The real flow rate in the G.C. oven is greater than that which was measured externally at ambient temperature because of the expansion of the gas in the hot oven. Hence:

$$\text{Real flow} = \text{total ambient flow} \times \frac{\text{oven temperature (K)}}{\text{ambient temperature (K)}}.$$

Plot log (retention volume) versus $\frac{1}{T\ (K^{-1})}$ and extrapolate to determine the retention volume at 20°C (293 K).

Column Measurements

Retention volumes can likewise be measured on G.C. columns packed with a known wieght of the adsorbent and using normal G.C. operating conditions. Report the results obtained by either method as specific retention volumes:

Specific retention volume = retention volume/weight of adsorbent.

DIRECT MEASUREMENT OF OVERALL EFFICIENCY

Simulate the sampling operation in the laboratory by injecting a known amount of the compound of interest, in aqueous or methanolic solution, into the end of the sample tube and drawing it on to the adsorbent with clean air, using the same flow rate and sampling time as would be employed in practice. Afterwards measure the amount of compound remaining on the tube by one of the above techniques, and from this calculate:

$$\text{Efficiency} \geqslant \frac{\text{amount detected}}{\text{amount injected}} \times 100 \text{ per cent.}$$

The inequality in this expression arises because the compound is injected at the beginning of the simulated sampling period. In practice a large portion of the sampled material would probably be collected in the later stages of a real sampling operation and this portion would be retained with correspondingly greater efficiency because it is purged for a shorter length of time.

An Application of the Method to the Measurement of Furfural Emissions from a Chemical Works

Extracts from a survey of furfural measurements in the atmosphere are reported here to illustrate the sensitivity and accuracy which is achieved with these techniques. The survey was carried out to study the dilution in the atmosphere of certain emissions from a factory stack which contained a significant amount of furfural.

Most samples were collected continuously for a period of 3 hours on Porapak Q adsorption tubes. Method (3) was used for the analysis and furfural was detected by selective ion monitoring, scanning the characteristic 97, 96, 95 and 67 m/e ion fragments on the mass spectrometer.

The calibration plot of the peak height for furfural relative to the external standard (injections on to the G.C. after each sample, of 200 ng of furfural dissolved in ethyl acetate) is shown in Figure 3. The points on the plot were

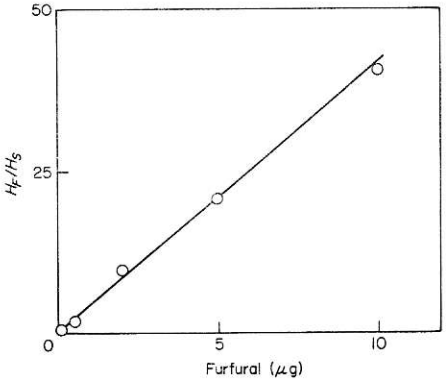

Fig. 3. Furfural calibration graph. H_F/H_S is the ratio of the furfural peak height of the sample to the peak height of a 200 ng furfural standard injected onto the Chromosorb column at 235°C.

mostly obtained on separate days over a period of one week and using three different adsorption tubes. The linearity and lack of scatter in the plot indicated that the technique was a reliable one.

TABLE I

OVERALL EFFICIENCY MEASUREMENTS FOR THE ADSORPTION OF FURFURAL ON A PORAPAK Q TUBE AND ITS TRANSFER TO THE COLUMN BY METHOD 3

Furfural injected, *μg*	Air flow rate, *ml/sec.*	Volume of air, *litres*	Efficiency of recovery, *per cent.*
3·0	6·1	66	87
0·2	4·1	44	100

This survey was carried out before the methods for retention volume measurements had been developed and the sampling technique was checked by making efficiency measurements. The two results of 100 per cent. and 87 per cent. obtained under different sampling conditions are presented in Table I and they showed that confidence could be placed in the above procedures. During the course of the survey further confirmation of the reliability of the technique was obtained by giving several tubes repeated blank measurements after their analyses, to check that a high tube to column transfer efficiency was being maintained. The results are given in Table II.

The dilution of the factory emissions in the atmosphere was calculated with the expression:

$$\text{Dilution} = \frac{[F_S]}{[F_A]-[F_B]}$$

where $[F_S]$ and $[F_A]$ were the concentrations measured at source and at the sampling site, respectively. $[F_B]$ was the background concentration, measured in an atmosphere independent of emissions from the factory. This background measurement was obtained by averaging the furfural concentrations for those samples which were taken when the wind was blowing the factory emissions away from the sampler. The concentration was very small, being in the range 1–2 $\mu g/m^3$, and to check that the measurements were valid two tubes were connected in series and city air was sampled through both of them. Analysis of the first revealed a typical background concentration of 1·9 $\mu g/m^3$. The second tube was found to contain no furfural (i.e. less than the limit of detection which was 0·1 $\mu g/m^3$ in that instance) and this effectively confirmed that the background measurements were genuine—and not a product of the analytical method.

TABLE II

THE EFFICIENCY OF THE DISCHARGE OF FURFURAL FOR THREE AIR SAMPLES COLLECTED ON PORAPAK Q

	The quantities of furfural, $F(\mu g)$, measured in successive clean runs					Efficiency of initial discharge $= (F_0/F_0+F_1+F_2+\text{etc.})\times 100$, *per cent.*
	F_0	F_1	F_2	F_3	F_4	
Sample A	3·1	0·13	0·036	0·0002	0·0000	99·5
Sample B	0·099	0·019	0·002	—	—	83
Sample C	0·42	0·011	0·009	0·0000	—	95

Some typical measurements of furfural concentrations and the dilutions of the factory emissions are reported in Table III for a series of eight 3-hourly samples.

TABLE III

FURFURAL CONCENTRATIONS AND STACK EMISSION DILUTIONS FOR A SERIES OF EIGHT 3-HOURLY SAMPLES

Sample time	Sample volume, *litres*	Total furfural concentration, mg/m^3	Dilution of stack gas in the atmosphere
15·50–18·50	85·3	0·37	600:1
18·50–21·50	55·0	0·040	5,800:1
21·50–00·50	77·7	0·022	11,000:1
00·50–03·50	47·0	0·011	25,000:1
03·50–06·50	66·4	0·005	71,000:1
06·50–09·50	74·3	0·001	∞
09·50–12·50	67·6	0·001	∞
12·50–15·50	60·8	0·001	∞

The sample site was 280 metres from the 52 metre high stack. Winds were 15 knots, varying from N.E. to E.N.E. overnight.

The concentration of furfural at source [F_S] was 220 mg/m³, and the background concentration, [F_B] was 0·0019 mg/m³.

The sampling site was set up at street level, 280 metres S.W. of the stack. The height of the stack was 52 metres and the winds were 15 knots N. Easterly varying E.N. Easterly overnight. This change in wind direction can be seen to coincide with the progressive fall in furfural concentrations.

Retention Volumes and Collection Efficiencies

In the air pollution survey outlined above, a considerable amount of time was spent in checking the reliability of the analytical techniques. Being a large survey, the cost of the time spent in confirming the techniques was only a small fraction of the total cost. Not all surveys are large enough to justify, on a cost and time basis, such extensive checking of the reliability of the techniques, especially as much of the work encountered is localised to one household or business premises. With an understanding of how a sample tube works and some experimental groundwork it is possible to predict the sampling conditions which will permit the sampling of any pollutant with a high collection efficiency.

The adsorption tube described in this paper can be looked upon as a very short chromatography column for which the air being sampled is the carrier gas. The organic pollutants in the air are adsorbed on the packing but, as with a chromatography column, they gradually travel through the tube and eventually the pollutants are purged out of it. If the subsequent analysis of the retained compounds is to be made quantitative, in terms of concentrations in the original sample, some knowledge of the retention volumes of the pollutants on the adsorbent packing is necessary. Using the methods described above, the specific retention volumes for styrene and pyridine on a Tenax G.C. adsorption tube were found to be 400 and 60 litre/g, respectively. These tube measure-

TABLE IV

SPECIFIC RETENTION VOLUMES AND ESTIMATED 75 PER CENT. RETENTION VOLUMES FOR 60/80 MESH TENAX G.C. OBTAINED FROM MEASUREMENTS ON A G.C. COLUMN

Compound	Specific retention volume, *litres carrier gas/ gramme adsorbent*	75 per cent. retention volume†, *litres*/0·25 *g*
Ethanol	1	0·2
Acetone	5	1
Benzene	25	3
Pyridine	70	9
Toluene	120	15
Styrene	500	60
Furfural	650	80
Naphthalene	2,000	250
Nicotine	15,000	2,000
Phenanthrene	15,000,000	200,000

† The 75% retention volume of a compound on a Tenax G.C. tube is the maximum volume of a carrier gas which can be passed through the tube at 20°C and still leave at least 75 per cent. of the compound retained in the tube.

ments show agreement within experimental error of the corresponding measurements on the G.C. column (Table IV). From this we have concluded that the retention volumes measured on a column can be used to estimate the retention volumes for an adsorption tube. This is a valuable conclusion since column measurements can be made more quickly and easily than can the direct measurements on the adsorption tube.

All of these results were based on measurements of the volume of carrier gas that flowed from the time of injection to the time of the G.C. peak maximum, which corresponds to the passage through the packing of approximately 50 per cent. of the compound injected. In a similar study, Pellizzari *et al.*[13] measured the specific retention volumes of compounds on Tenax G.C. They also found close agreement between the results obtained on a Tenax G.C. column and on a Tenax G.C. tube.

The collection efficiency of a sample tube, defined as:

$$\text{Collection efficiency} = \frac{\text{amount retained}}{\text{amount in original sample}} \times 100 \text{ per cent.}$$

depends for any given compound on the retention volume of that compound, and it is affected by the length of the sampling period. The longer the sampling period, or the smaller the retention volume, the more the compound elutes from the tube, and the collection efficiency is reduced.

Although it would be difficult to determine accurate collection efficiencies for a particular sampling operation, it is possible to calculate the minimum collection efficiencies. Butler and Burke[15] have demonstrated precise, but complex methods for determining the maximum sampling volume which would ensure at least 99 per cent. recovery of any given compound. But such data is available for only a few compounds. We have taken a simpler, if less precise, approach for estimating the maximum sample volume for each compound which still

ensures a high collection efficiency for that compound. The figure of 99 per cent. collection efficiency, chosen by Butler and Burke, is rather high in view of the other errors involved in most practical air sampling exercises and we choose to aim for a minimum collection efficiency of 75 per cent. For the purpose of the calculations, first assume that the specific retention volumes reported in Table IV correspond to the passage of 50 per cent. of each compound over 1 g of Tenax G.C. in a tube. Further assume that the tube is only a very poor chromatography column such that if a compound is injected on to it while air is being drawn through, then the compound would be purged off the tube at a virtually constant rate. After the passage of one half of its specific retention volume, therefore, 25 per cent. of the compound would have been eluted and 75 per cent. would have been retained on the 1 g tube. For a tube containing not 1 g but 0·25 g, the 75 per cent. retention volume would be one eighth of its specific retention volume. The 75 per cent. retention volumes calculated in this way for the 0·25 g tubes are shown in the third column on Table IV.

The two assumptions that were made for these calculations permit a considerable margin of error since:

(a) the discharge of adsorbed material from the tube during sampling does not occur at a constant rate but approximates to the form of a very broad Gaussian peak, so that the calculations tend to underestimate the collection efficiencies;

(b) these calculations apply only to the pollutants adsorbed at the beginning of the sampling period—material adsorbed at later stages of sampling would suffer correspondingly less elution, and the overall efficiency would again tend to be greater than calculated.

In view of the limited accuracy being aimed at in this approach (i.e. a possible error of up to 25 per cent. in the least retained compound) it is not necessary to carry out an independent determination of the retention volume for every pollutant not listed in Table IV. Knowing the position of the pollutant in the sequence of elution from Tenax G.C., it is possible to estimate its retention volume by comparison with those compounds in Table IV which elute before and after it.

The significance of these considerations can be understood by reference to an air sample data sheet. One such is illustrated in Table V for a sample of household air which was taken following complaints from the occupants of bad smells and a feeling of nausea. The problem was of a spasmodic nature and the sampling equipment was left with the householder for her to collect the sample. The sample volume was approximately the same as the 75 per cent. retention volume of toluene, for which the collection efficiency would therefore have been 75 per cent. or more. The concentrations of toluene and the compounds eluting after it were calculated by the method described in the experimental section and are listed in the 4th column of Table V. It is important to note that these concentrations are only approximate in absolute terms, since they were derived by assuming a similar and linear calibration for all compounds with respect to the external standard. Nevertheless, it was possible to make a reliable comparison of the results with those of other air samples analysed by the same procedure. When this was done, the sample was found to have had an un-

TABLE V

A LABORATORY DATA SHEET

Type of Sample: Domestic air
Peculiarities: Occupants complained of "petrol-like fumes" which begin to appear in the evening and then disappear by lunchtime the following day. Smell disappears in damp weather but is worst during long hot spells.
Adsorbent: Tenax G.C. Weight: 0·25 g Tube: T.G.C. 2
Volume: 8·6 litre Date: 28 August 1977 Time: 9.55 a.m.
Column: Tenax G.C. 2 m × 2 mm Flow: 20 ml/min
Temperature program: 50–350°C, 10°C/min Sensitivity: 2, 10^{-6}/1, 20 mV
Upper quantitative limit: † Peak 25A Lower quantitative limit: † Peak 9
Standardisation relative to: the peak height of a 10 μg injection of ethyl acetate. The results are reported as (mg/metre^3)‡ in the original sample.

Peak	Temperature, °C	Compound	Approximate concentration‡, *mg/ml*
3	117	*n*-pentane	—
4	121	*cis*-2-pentene or trans-2-pentene	—
6	141	Hexane	—
8	158	Benzene and *n*-heptane	—
9	176	Toluene and a paraffin, C_8H_{18}	3·9
10	196	Xylene	2·7
11	203	Xylene	0·49
12	213	1-methyl-3-ethyl benzene	1·2
13	219	Trimethyl benzene	0·46
14	224	Probably 1,2-diethyl benzene	0·14
14A	228	1,4-dimethyl-2-ethylbenzene	0·09
16	255	Naphthalene and a paraffin, $C_{14}H_{30}$	0·040
18	270	Paraffin, mol. wt. 226, $C_{16}H_{34}$	0·061
20	300	Diethyl phthalate	0·11
21	307	Unidentified, mol. wt. 212	0·12
23	315	Paraffin, mol. wt. 256, $C_{18}H_{40}$	0·22
24	323	Paraffin	0·86
25	328	Paraffin, mol. wt. 338, $C_{24}H_{50}$	1·7
25A	332	Phenanthrene	0·06
27	335	Paraffin, mol. wt. 352, $C_{25}H_{52}$	2·8
28	341	Paraffin, mol. wt. 366, $C_{26}H_{54}$	3·5
29	348	Paraffin, mol. wt. 380, $C_{27}H_{56}$	3·4
30	350 (+0·6 min)	Paraffin, mol. wt. 394, $C_{28}H_{58}$	3·0
31	350 (+1·2 min)	Paraffin, mol. wt. 408, $C_{29}H_{60}$	2·0
32	350 (+1·9 min)	Paraffin, mol. wt. 422, $C_{30}H_{62}$	1·5
33	350 (+2·8 min)	Paraffin, mol. wt. 436, $C_{31}H_{64}$	0·63
34	350 (+3·8 min)	Paraffin, mol. wt. 450, $C_{32}H_{66}$	0·20
35	350 (+4·6 min)	Paraffin, mol. wt. 464, $C_{33}H_{68}$	0·09
36	350 (+6·1 min)	Paraffin, mol. wt. 478, $C_{34}H_{70}$	0·02

† The quantitative limits indicate the part of the analysis for which more than 75 per cent. of the sample was recovered.
‡ For the method of calculation see the experimental section.

usually high level of organic contamination. Several sources of pollution were suggested to the Environmental Health Officer, namely tar fumes from building operations, leakage of fumes from oil fired central heating, or fumes from a garage. The investigation is continuing.

This semi-quantitative approach is adequate for many investigations, but if necessary more accurate data can be provided by calibrating the compounds of interest against the external standard. We have found that the approximate measurements do not differ from their calibrated concentrations by more than a factor of 3 and usually by less than a factor of 2, provided that the chromatogram peak heights are not excessively broad and do not suffer severe tailing.

The discussion so far has been concerned with the problem of estimating sampling efficiencies for volatile compounds. It is also possible that this efficiency may be reduced for the less volatile material because of poor transfer efficiency from the sample tube to the G.C. column. The efficiency of the Tenax tubes was tested for 43 μg of phenanthrene (B.P. = 340°C) and the transfer efficiency with Method (1) was 90–100 per cent. It can be assumed that more volatile compounds would be transferred with this or greater efficiency. The exceptions to this would be unstable or reactive compounds which may suffer thermal decomposition or reaction during the transfer stage, but using the methods described here, this should be no more of a problem than it is in the gas chromatographic analysis itself.

Phenanthrene is the most strongly retained compound for which the efficiency of sample recovery has yet been checked. If more strongly retained compounds need to be measured quantitatively their transfer efficiencies must also be measured.

GENERAL COMMENTS

Tenax G.C. has advantages over Porapak Q because of its thermal stability and lack of column bleed, and it has been the most widely used adsorbent in our work. However, Porapak Q has the better sampling capacity[15] and is considerably cheaper. The bleed from Porapak Q consists of ethyl-styrene and related compounds and these can sometimes cause difficulty during chromatographic analysis if they overlap with the compounds of interest. There were no such difficulties in the use of Porapak Q for the furfural survey.

Of the transfer procedures, Method (1) is preferred since it permits the transfer of a wide range of compounds with a minimum of procedure; but with other G.C. systems Methods (2) and (3) may be more appropriate.

The sample tubes were designed to fit into Pye Unicam $\frac{1}{4}$ inch couplings, which we find particularly convenient. However, they do require a certain amount of glass-blowing expertise in their construction. Where this is not available it should be possible to construct a similar sample tube from a straight length of glass or stainless steel tube, and make the attachment to the G.C. via Swagelok couplings.

These techniques are not limited to use with a mass-spectrometer. More conventional G.C. detectors have been used extensively in this type of work,[4,6,13,16,19] and they are particularly suited to investigations where there are only a few major compounds of interest. Halliday[17] has found that adsorption tubes of similar design to those described here were suitable for the G.C. analysis of anaesthetic vapours in hospital operating theatres. The compounds of interest included low molecular weight alcohols and halothane and they were analysed on a Pye Unicam 104 G.C. with a flame ionisation detector. Conventional G.C. systems can also be used where there is one major source of pollution which gives a characteristic chromatogram on the G.C.

Conclusions

The techniques described in this paper permit the taking of time-averaged air samples and spot samples for a wide range of compounds, and can be used for

monitoring air pollution to test for compliance with the Government Guidance Note on Threshold Limit Values.

They do not require trained personnel for the sampling operation itself, and in the event of spasmodic complaints of air pollution the equipment can be loaned out to a member of the public to take the sample.

The apparatus costs relatively little to construct and is suitable for use with any G.C. system.

When necessary the techniques can be made very accurate and sensitive.

For nearly all of public health work, which does not require extremes of accuracy, we have established simple procedures for the quantitative assessment of the analyses with an adequate level of accuracy.

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The Gas Phase Extraction and Analysis of Volatile Organic Pollutants in Water Using a Tenax G.C. Adsorption Tube

B. I. Brookes, S. M. Jickells and R. S. Nicolson

Department of the Regional Chemist, Strathclyde Regional Council, 8 Elliot Place, Clydeway, Glasgow

A gas phase stripping technique is described for the concentration and subsequent measurement of trace quantities of volatile organic pollutants in water. The compounds are extracted on to a Tenax G.C. adsorption tube. The sample is transferred to a Tenax G.C. column by thermal desorption and analysed by temperature programmed G.C. or G.C./M.S. The factors governing the quantitative interpretation of the results are discussed and a sensitivity of 0·1 μg/litre is reported for the analysis of styrene in 250 ml of an aqueous sample.

The use of adsorbents for the extraction of organic pollutants from water, prior to analysis, has certain advantages over the techniques of liquid/liquid extraction since it permits a large concentration factor, without contamination, and at the same time it allows the concentration of volatile compounds, without significant loss.

The extraction may be carried out by:

(a) gas phase stripping techniques[1–4] in which a gas is passed through the sample and carries the volatile species on to the adsorbent, or,
(b) headspace analysis[5,6,7] in which the headspace vapours of the water sample are drawn through the adsorbent, or,
(c) direct passage of the aqueous sample through an adsorbent bed.[5]

The pollutants may then be removed from the tube by liquid extraction[1] or by thermal desorption.[2–4]

The principles involved in the operation of the gas phase stripping techniques are related to those for atmospheric sampling with adsorption tubes, and much of the groundwork involved in determining collection efficiencies and retention volumes is the same for both. It is a simple matter therefore, to extend the use of adsorption tubes, designed for air sampling, to include the extraction of organic pollutants from water. However, it is important to remember that gas phase stripping techniques introduce a new factor into the quantitative interpretation of the results of adsorption tube analyses. This is the efficiency with which the pollutants, particularly the less volatile pollutants, are removed from the aqueous sample.

The gas phase stripping technique described here uses the sample tube and analytical procedures described in the previous paper.[8]

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Experimental

APPARATUS (see Figure 1)

The sample is contained in a Quickfit flask of appropriate size which is supported in a boiling water bath. Nitrogen is used as the stripping gas and it is cleaned by passage through a 30–60 mesh activated charcoal filter, before being bubbled through the sample via a porous glass frit. The gas and vapours pass through a double walled condenser and through the adsorption tube. There is the possibility that the less volatile components of the sample would be retained

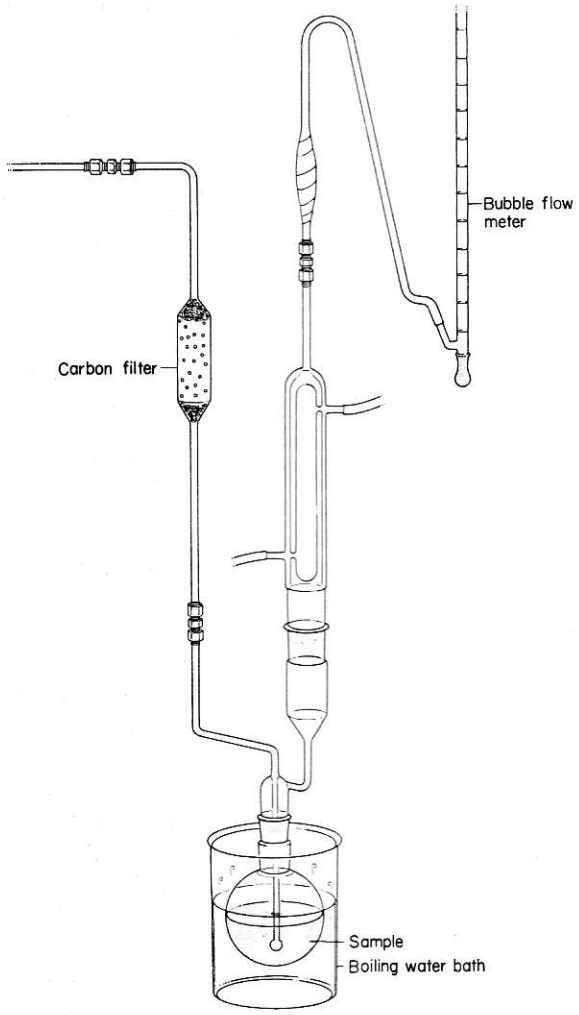

Fig. 1. The apparatus for the transfer of organic volatiles from the sample to the adsorption tube.

by the wall of the condenser and so it is advisable to clean the system between analyses by steaming as in the method described below. The use of rubber bungs and plastic or rubber tubing should be avoided in the construction of the

apparatus, but connections can be made with ground glass joints, Drallim couplings, or Swagelok couplings fitted with silicon rubber O-rings, as appropriate.

The adsorption tube and analytical techniques have already been described in detail.[8] The adsorption tube contained 0·25 g of 60–80 mesh Tenax G.C. packed into a tube with an internal diameter of 7 mm. Analyses were carried out with a 2 metre × 2 mm, 60–80 mesh Tenax G.C. glass column fitted in a Pye Unicam series 104 G.C. oven. This was interfaced to a VG Micromass 16B mass spectrometer which could be used in the usual fast scanning mode, or as a selective ion detection system. During the analysis the column was temperature programmed from 50°C to 350°C at 10°C pm.

METHOD

Steaming out the equipment. Drain the condenser of its cooling water and half fill the sample flask with distilled water. Connect the flask to the apparatus and pass a slow stream (30 ml/min) of nitrogen. Boil the water in the flask for 10 minutes to steam out any organic contamination, and let the apparatus cool with the nitrogen still flowing.

Extraction technique. Empty the sample flask and put in a measured amount of the sample (10–250 ml, depending on the amount available and the expected level of contamination). Pass cooling water through the condenser, fit the adsorption tube to the apparatus, and attach the sample vessel. Increase the nitrogen flow rate to 2 ml/sec. (7·2 litre per hour) and raise a boiling water bath about the sample. After 1 hour, or less if the 75 per cent. retention volumes of the compounds of interest are likely to be exceeded, remove the tube and the water bath and turn off the nitrogen flow.

Analysis. Analyse the sample by one of the thermal desorption and G.C. methods described in the previous paper,[8] and repeat the extraction and analysis using the purged sample and the same sample tube. If the repeat run is clean, this indicates that all of the contaminants were purged from the sample in the first run, and that the tube can be set aside ready for further use. If the repeat run still shows signs of contamination then, at the discretion of the operator, further extractions can be carried out—always finishing with a blank run from the purged sample, or, if necessary, from distilled water.

Results and Discussion

One of the frequent uses for this technique in the authors' laboratory has been the analysis of styrene in drinking water after the installation of a fibre glass tank. To illustrate the method, the results are given in Table I of two analyses of a drinking water supply in Glasgow, 250 ml samples of which were extracted on to adsorption tubes. The first sample, taken shortly after the installation of the tank, contained a significant amount of styrene, and its odour and taste could be detected in the water. There was a much smaller level of styrene in the second sample, taken 11 weeks after installation—the apparent increased level of the other constituents results from the use of the instrument in a more sensitive

mode. Most of the other compounds listed in Table I have also been reported in the literature as common components of drinking water from city supplies.[3]

The volume of stripping gas used in the extraction procedure, 7·2 litres, was well within the 75 per cent. retention volume[8] of 60 litres for styrene on the adsorption tube, and so the collection efficiency was expected to be very high. However, it was necessary to check the efficiency with which the styrene was extracted from the sample. To do this a solution of 0·04 mg/litre styrene in water was prepared by injecting 25 μl of 0·4 g/litre styrene in methanol, i.e. 10 μg styrene, into 250 ml of distilled water. Two adsorption tubes were connected in series and the sample extracted by the normal procedure.

TABLE I

TWO ANALYSES OF A GLASGOW DRINKING WATER WHICH HAD BEEN CONTAMINATED WITH STYRENE FROM A FIBRE GLASS TANK

Compound	Estimated concentration, $\mu g/litre$†	
	1 week (approx.) after installation	11 weeks (approx.) after installation
Chloroform	—	2·0
Tetrahydrofuran	—	0·9
Bromo-dichloro-methane	—	0·9
Dibromo-chloro-methane	—	0·2
Styrene	200	<0·1
1,3-butanediol	2	—

† The styrene concentration was measured by calibration, the other compounds were quantified by assuming they had a similar calibration to that of styrene.

Analyses were carried out on the first and second tubes, and on a repeat extraction of the purged sample. Detector calibration was carried out with 25 μl injections of the styrene in methanol solution using the same syringe as was used to prepare the aqueous sample. In this way the absolute error of the syringe calibration did not affect the efficiency calculations. The only important error was the reproducibility of the syringe, which was ± 3 per cent. The results are given in Table II.

TABLE II

	First tube	Second tube	Repeat extraction	Total
Styrene (μg)	9·6	0·42	0·032	10·05

From this it can be seen that the efficiency of the analysis on the first tube was

$$9{\cdot}6/10{\cdot}05 \times 100 = 96 \text{ per cent.}$$

The efficiency of the vaporisation of the styrene in the first extraction was

$$(10{\cdot}05\text{–}0{\cdot}032)/10{\cdot}05 \times 100 = 99{\cdot}7 \text{ per cent.}$$

and the collection efficiency of the vaporised material on the first tube was

$$9{\cdot}6/(9{\cdot}6 + 0{\cdot}42) \times 100 = 95{\cdot}8 \text{ per cent.}$$

At 96 per cent. the overall efficiency of the first analysis was very high, and this is completely satisfactory for most purposes.

The results show that the main loss of styrene arose from the 95·8 per cent. collection efficiency, rather than the vaporisation efficiency, which was 99·7 per cent. It ought to be possible to improve this technique still further by reducing the volume of the purging gas. A small reduction should have little effect on the efficiency of vaporisation, but it could improve the collection efficiency by reducing the amount of styrene that elutes from the tube.

This work was carried out using the mass spectrometer in its fast scanning mode and the sensitivity for the 250 ml sample was estimated to be 0·1 μg/litre. A similar sensitivity would be expected with a flame ionisation detector. These techniques have also been used for the measurement of paint volatiles in drinking water and for the measurement of various forms of industrial contamination in sewer waters—including successful analyses for tetrahydrothiophene and for a tar based disinfectant.

Conclusion

The procedure described here provides a sensitive method of identifying and quantifying volatile pollutants for public health and pollution control investigations in situations where analyses by conventional methods would be tedious and unreliable.

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The Quality of Ham

Report by the Liaison Group for Nationally Co-ordinated Sampling

A. J. HARRISON (CO-ORDINATOR)

7 Redcross St, Bristol BS2 0BA

The concept of nationally co-ordinated sampling developed from sampling programmes set up to improve efficiency of local enforcement procedures following Local Government Reorganisation. The success of these prompted liaison between the Association of Public Analysts and the Society of County Consumer Protection Officers to consider the feasibility of a similar approach at national level. As a consequence, following the report of a Working Group, the national system was established and the Association of London Chief Environmental Health Officers agreed to join the Scheme which was initiated in October 1977.

The objectives of the Scheme are to investigate particular areas of interest with a view to producing data for specific purposes to meet local, research, national and international needs.

It is not intended that details of all projects will be published. However, the Liaison Group feel that, in certain instances, the conclusions drawn are of sufficient significance to merit this. The project concerning the quality of ham reported below was judged to be in this category.

Project—Ham Quality

In all, 271 samples of ham, sub-divided as shown here, were analysed and reported in this survey:

(1) ham sold off the bone, 45 samples;
(2) prepacked sliced ham, 101 samples;
(3) non-prepacked sliced ham, 125 samples.

Samples submitted by enforcement officers together with details concerning price, origin, method of marketing, etc., were analysed by Public Analysts for apparent meat content. The analysis was carried out by the Stubbs and More procedure[1,2] and the apparent meat content calculated as raw pork using the mean nitrogen content of fat-free raw pork as 3·45 per cent. recommended by the Society for Analytical Chemistry.[3]

Standards

There are no statutory standards for ham other than those provided by the general provisions of the Food and Drugs Act.

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One clear conclusion from the survey is that the nature of ham in the traditional sense, i.e. ham off the bone, is changing toward a product with a higher water content. In the vast majority of cases where ham is sold prepacked or loose as a sliced product, the change is possibly irreversible. There appears to be no significant price advantage to the consumer, as a consequence of which it costs around 15 pence for the water in each pound of the moist product.

Several analysts have indicated that they have given adverse certificates in relation to some of the samples analysed by reason of added water. However, even if the generous allowance is made that the product should calculate out at 100 per cent. raw meat equivalent. i.e. as raw pork, plus a 5 per cent. allowance for the incorporation of curing/emulsifying salts, at least 64 per cent. of the products could be criticised.

General Conclusions

1. There is ample evidence of the addition of extraneous water to ham of between 5 and 25 per cent., the most common addition being around 15 per cent.
2. The quality of traditional ham has deteriorated significantly.
3. If the degree of deterioration is to be arrested, urgent steps must be taken to establish acceptable standards.
4. It may well be that the so-called "moist" ham is now so well established that separate standards will have to be negotiated to meet this.
5. Whatever action is decided, it is important that it is taken promptly to prevent the purchaser from continuing to be misled as to the quality of the product offered.

Ham "Off-the-Bone"

1. Forty-five well identified products were submitted. Consideration of meat content against price showed that there were two distinct products on the market, when judged against 100 per cent. raw meat equivalent as the minimum anticipated for ham off the bone (Appendix C).

(a) Traditional hams	Raw meat equivalent	—105–136 per cent.
	Price range	—£1.00–£1.80 per lb
	Average price	—£1.34 per lb
	No. of samples	—23
(b) Wet hams	Raw meat equivalent	—79–104 per cent.
	Price range	—£1.10–£1.80 per lb
	Average price	—£1.39 per lb
	No. of samples	—22

2. Thirty samples (66 per cent.) contained not more than 5 per cent. "added water" and, after allowance for curing/emulsifying salts (up to 4 per cent.), might be judged as genuine (Appendix A). However, only 23 (51 per cent. of samples) had raw meat equivalents of over 105 per cent. and were therefore likely to have been traditional hams (Appendix B).

3. The most commonly occurring added water content in the wet ham group (15 samples, 33 per cent.) was in the range 16–20 per cent., with an average of 16·4 per cent. Allowing for an average amount of added curing/emulsifying salts of 4 per cent., this represents about 12 per cent. of true added water. With an average price of about £1.40 per lb, this represents about 17 pence for added water per lb of product. This is a valid statistic since 56 per cent. of hams purchased had raw meat equivalents of over 100 per cent. and could be purchased within the same price range (Appendix C).
4. It is concluded therefore that "off-the-bone" hams are "deteriorating in quality" or "increasing in succulence", depending on the point of view, as a consequence of modern curing processes which, in spite of the weight gained, do not result in a more competitive price being offered to the consumer. There are undoubtedly two qualities of "off-the-bone" ham being offered for retail sale within the same general price range.

Prepacked Ham

1. Twenty (22 per cent.) of the samples submitted contained not more than 5 per cent. of added water and, after allowance for curing/emulsifying salts, could be judged as genuine, although of these, only 4 (4 per cent.) were likely to have been traditional hams (Appendices A and B).
2. Of the remaining 78 per cent., most lay in the range 16–20 per cent. of added water, with an average of 14·7 per cent. After an allowance for curing/emulsifying salts of 4 per cent., this leaves an average added water content of 11 per cent. The price of these products is around £1.40 per lb, representing about 15 pence for added water per lb of product.
3. In the case of 75 per cent. of the returns under prepacked ham it was possible to ascertain the country of origin. From these, it is apparen that in the U.K. there is a spread of quality between 76–100 per cent. raw meat equivalent calculated on the basis of this exercise. Dutch hams most commonly contain around 81–85 per cent. and, whilst the range is similar to the English product, Dutch hams tend to have about 5 per cent. lower raw meat equivalent on average (Appendix D).

   The nine Danish products tended to be similar if not slightly better than both the Dutch and English products. The three products with over 110 per cent. meat content listed under English in Appendix D were home produced hams and gammons.
4. Cured pork shoulder (22 samples) included here as "Shoulder Ham" had an average raw meat equivalent of 81·6 per cent. with a range of 71–95 per cent. After allowance (4 per cent.) for curing/emulsifying salts, this represents about 14 per cent. added water with an average price of £1.24 per lb, or about 17 pence for added water per lb of product. One exceptional shoulder ham was designated Royal Wiltshire and had a raw meat equivalent of 115 per cent. and was selling for 96 pence per lb.
5. One analyst reported that, in two instances, free water representing 5·3 per cent. and 7 per cent. by weight of the samples was found in the pre-pack container.

Non-Prepacked Ham

1. One hundred and twenty-five samples were identified as belonging to this category. Once again, consideration of price against meat content showed evidence of two different commodities on the market (Appendix C).

   (a) Traditional hams — Apparent meat content range—105–140 per cent.; Price range —£0.70–£1.80/lb†; No. of samples —25

   (b) Wet hams — Apparent meat content range —68–105 per cent.; Price range —£0.60–£1.80/lb; No. of samples —100

2. Forty-eight samples (38 per cent.) contained not more than 5 per cent. added water and, after allowance for curing/emulsifying salts, could be judged as genuine (Appendix A). However, of these, only 25 (20 per cent.) had meat contents over 105 per cent. and were likely to have been traditional hams (Appendix B).
3. Of the remaining 62 per cent. of samples, most lay in the range 21–25 per cent. added water, with an average of 16·4 per cent. After an allowance for curing/emulsifying salts, this leaves an average added water content of 12 per cent. The price of these products is around £1.11 per lb, representing about 13 pence per lb of product for added water.
4. Other than for speciality hams such as Parma, Westphalian, etc., priced at over £2.00 per lb, the price of non-prepacked genuine hams on average is about £1.35 per lb compared with £1.11 per lb for wet ham.

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Appendix A

ADDED WATER,
i.e. (100 — raw meat equivalent)‡

Water, *per cent.*	Off-bone	Prepacked	Non-prepacked	Totals
0–5	30	20	48	98
6–10	2	19	19	40
11–15	3	23	16	42
16–20	7	26	14	47
21–25	3	11	20	34
26–30		2	7	9
31–35			1	1
Totals	45	101	125	271
> 5 per cent.	33 per cent.	80 per cent.	62 per cent.	64 per cent.

† Three speciality hams not included (see Appendix C).
‡ No allowance for addition of curing or emulsifying salts.

Appendix B

RAW MEAT EQUIVALENTS

Meat, *per cent.*	Off-bone	Prepacked	Non-prepacked	Totals
61–65				
66–70			2	2
71–75		5	8	13
76–80	5	13	24	42
81–85	6	28	14	48
86–90	3	19	17	39
91–95	2	18	16	36
96–100	4	9	15	28
101–105	2	5	4	11
106–110	6		7	13
111–115	7	3	4	14
116–120	4	1	3	8
121–125	2		5	7
126–130	2		3	5
131–135	1		1	2
136–140	1		2	3
Totals	45	101	125	271
No. >100 per cent.	25	9	29	63
Per cent. >100 per cent.	55·6 per cent.	8·9 per cent.	23·2 per cent.	23 per cent.

Appendix C

PRICE PER POUND

	Off-the-bone			Prepacked			Non-prepacked			
Price/lb	100 per cent. +†	100 per cent. —†	Totals	100 per cent. +	100 per cent. —	Totals	100 per cent. +	100 per cent. —	Totals	Grand Totals
£0·60–0·70								3	3	3
£0.71–0.80					1	1	1	9	10	11
£0.81–0.90					1	1	1	7	8	9
£0.91–1.00				1	3	4	1	10	11	15
£1.01–1.10	1		1		2	2	1	13	14	17
£1.11–1.20	5	1	6	2	2	4	4	19	23	33
£1.21–1.30	3	4	7	1	14	15	4	7	11	33
£1.31–1.40	7	6	13	2	19	21	7	9	16	50
£1.41–1.50	4	1	5	1	19	20	6	10	16	41
£1.51–1.60	3	6	9	2	23	25	3	4	7	41
£1.61–1.70	1	1	2	1	2	3				5
£1.71–1.80	1	1	2		4	4	1	1	2	8
£1.81–1.90								1	1	1
£1.91–2.00										
£2.40				1		1				1
£3.38							1		1	1
£3.60							1		1	1
£5.00							1		1	1
Totals	25	20	45	11	90	101	32	93	125	271

† 100 per cent. + = raw meat equivalent of 100 per cent. or greater;
100 per cent. — = raw meat equivalent of less than 100 per cent.

Appendix D

ANALYSIS OF RESULTS FOR RAW MEAT EQUIVALENT OF PREPACKED SLICED HAMS ACCORDING TO ORIGIN

Raw meat, *per cent.*	English	Dutch	Danish	West German	Rumanian	Polish	Totals
61–65							
66–70							
71–75	1	3	1				5
76–80	6	3					9
81–85	10	7	3				20
86–90	9	1	4				14
91–95	8	3	1		1	1	14
96–100	6	1					7
101–105	3			1			4
106–110							
111–115	2						2
116–120	1						1
Totals	46	18	9	1	1	1	76

The foregoing paper is being published, by agreement between the liaising bodies, in *The Monthly Review* (the Journal of the Institute of Trading Standards Administration) and *Environmental Health* (the Journal of the Association of Environmental Health Officers) as well as in this Journal.

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Determination of Beryllium in Ambient Air Particulates

P. C. ENSOR

Scientific Laboratory, Environmental Department, Birmingham District Council, 150 Great Charles Street, Birmingham B3 3HT

A method is described for the determination of beryllium in airborne particulates retained on MF Millipore filters. After wet digestion of the filters and extraction of the beryllium as the trifluoroacetyl acetonate, a G.L.C. method is used enabling 1×10^{-12} grammes of beryllium to be detected. The detection limit in air is 0·0001 microgramme per cubic metre but this could be lowered considerably using alternative sampling techniques. Recovery of added beryllium is satisfactory and the results from several hundred analyses range from <0·0001 to 0·0015 microgrammes per cubic metre of air.

Beryllium is a highly toxic element with a Threshold Limit Value in air of 2 microgrammes per cubic metre[1], whilst there is a Short Term Exposure limit of 25 microgrammes per cubic metre. It is known that very small amounts inhaled over long periods can cause severe respiratory damage.[2] Although work has been carried out in the U.S.A. to determine the levels of beryllium in air where amounts ranging from 0·000027 to 0·00049 microgrammes per cubic metre have been found,[4,5] there are few figures available for these levels in the United Kingdom. The U.K. West Midlands area is highly industrialised and contains several factories which use or process beryllium. Consequently, it was decided in 1976 to commence a general survey of the level at which the metal is present in the air of Birmingham, particularly in the vicinity of a large non-ferrous metal extraction and fabrication complex on the north side of the city, to supplement data already obtained over many years for six heavy metals (Cd, Zn, Pb, Cr, Cu, Ni).

The determination used is the extremely sensitive G.L.C. method adopted by other workers,[3,4,5] but with modifications detailed below. The principle of the method involves the wet destruction of the Millipore filter on which the particulate matter is collected, followed by extraction of the chelate formed by beryllium with trifluoroacetylacetone in solution in toluene and subsequent injection of this chelate onto a G.L.C. column.

Experimental

APPARATUS

McCartney bijou bottles $\frac{1}{4}$ oz (7 ml). These are readily available and of low cost. The aluminium caps are replaced with subaseal silicone stoppers (size no. 30) and the bottles are silanized before use.

Shaker. Variable speed model (A Gallenkamp & Co. Ltd.).

Clamp for holding McCartney bottles. Designed to hold eight bottles, it is

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constructed from two pieces of wood $\frac{1}{2}$ inch $\times$ $\frac{1}{2}$ inch $\times$ 6 inch (13 $\times$ 13 $\times$ 152 mm) screwed and sealed together to form an inverted letter T. The vertical shaft is used for clamping in the shaker and along the horizontal portion are screwed 5/8 inch (16 mm) Terry clips, four on each side. The whole clamp including the clips is painted with a polyurethane varnish for protection.

5–50 microlitre Finnpipette or similar microlitre pipette.

0·2 ml micropipette, 1 ml safety pipette, Pasteur pipettes with rubber teats.

50 ml Kjeldahl flasks.

Distillation apparatus.

GAS-LIQUID CHROMATOGRAPHY

Pye Unicam G.C.V. chromatograph fitted with an electron capture detector and connected to a Philips PM 8220 recorder.

Column: glass (1·5 metres $\times$ 4·0 mm i.d.) packed with 3 per cent. SE30 on 100–120 mesh Diatomite CQ.

Operating conditions: column temperature = 130°C;
injection port temperature = 150°C;
detector temperature = 200°C.

Carrier gas flow rate: 70 ml of nitrogen per minute.

Detector current: 4×10^{-10} amperes.

Attenuation range: 128 or 256.

REAGENTS

Use Analytical Reagents and glass distilled water throughout. All glassware should be thoroughly rinsed with 3N sulphuric acid followed by distilled water before use.

1. *Nitric acid*, S.G. 1·42.
2. *Sulphuric acid solutions*, 50 per cent. v/v and 3N.
3. *Perchloric acid*, S.G. 1·54.
4. *Sodium hydroxide solutions*, 50 per cent. w/v and 3N.
5. *Alkaline wash solution.* Dilute 2 ml of 3N sodium hydroxide solution to 50 ml, add 5 g of anhydrous sodium sulphate, shake to dissolve, and make up to 100 ml with water.
6. *Toluene.*
7. *Methyl red indicator solution.*
8. *Beryllium standard solutions.* (a) 1,000 microgrammes per ml. Dissolve 1·967 grammes of beryllium sulphate tetrahydrate in water, add 10 ml of 3N sulphuric acid solution and make up to 100 ml with water in a volumetric flask. (b) 10 microgrammes per ml. Pipette 1·00 ml of standard beryllium solution (1,000 microgrammes per ml) into a 100 ml volumetric flask, add 10 ml of 3N sulphuric acid solution and make up to the mark with water. This solution is stable if stored in a polythene bottle.
9. *Buffer solution.* Dissolve 5·15 grammes of disodium-EDTA-dihydrate and 85 grammes of sodium acetate trihydrate in 400 ml of water. Add 5 ml of glacial acetic acid, mix and adjust the pH of the solution to 5·7 $\pm$ 0·1

at 20°C by the dropwise addition of glacial acetic acid or 50 per cent. sodium hydroxide solution. Finally, make up to 500 ml with water, mix and check the pH.

10. *1:1:1 Trifluoroacetylacetone (T.F.A).* Obtainable from B.D.H. Ltd., Poole, Dorset. This is usually impure as received but purification is achieved during the following distillation procedure.
11. *T.F.A. chelating solution* 0·04 M. A simple distillation apparatus, without thermometer, is required using, for 40 ml quantities, a 100 ml Quickfit flask. Into the flask place 50 ml of toluene and a few anti-bumping granules. Using the 0·2 ml micropipette add 0·2 ml T.F.A. to the toluene and mix. Distil exactly 40 ml into a graduated stoppered cylinder, using a hotplate and transfer the well mixed distillate to a polythene bottle. This solution is stable for at least one month if stored in a refrigerator.

PROCEDURE

(A) Digestion

The digestion of the filters can be carried out using perchloric or sulphuric acid.

Insert the exposed Millipore filter (see Discussion) carefully down the neck of the Kjeldahl flask. Add 2 ml of perchloric acid and 5 ml of nitric acid, boil down to white fumes of perchloric acid and maintain at this temperature for about 5 minutes. Allow to cool. To ensure absence of nitrous fumes add 10 ml water and again boil down to fuming. The digestion with sulphuric acid is similar but substituting 1 ml of 50 per cent. v/v sulphuric acid for the 2 ml of perchloric acid and completing the wet digestion with the addition of a few drops of nitric acid in the usual way. Whichever digestion is used, after removal of nitrous fumes, cool the residue, wash into a calibrated 25 ml flask, make up to volume with water, mix and filter through a 7 cm Whatman no. 41 filter paper if necessary.

(B) Determination

Pipette 1 ml of digest into a McCartney bottle, add one drop of methyl red indicator followed by 3N sodium hydroxide solution until one drop changes the colour of the indicator. Add 1 ml of buffer solution, mix and, using the 1-ml safety pipette, add 1 ml of chelating solution.

Insert the stopper, ensuring that the neck of the bottle is dry, and place the bottle in the clamp. Shake vigorously for 1 hour and then allow to separate. The solutions are stable and can be left at this stage if necessary, but the following steps should be carried out just prior to injection.

Remove the stopper and, with a Pasteur pipette fitted with a rubber teat, carefully remove all the lower aqueous layer and discard. Add 2 ml of alkaline wash solution, re-stopper and shake vigorously by hand for exactly 30 seconds. Allow 1 minute for the upper organic layer (which should be clear and colourless) to separate, then remove all the alkaline wash solution with a second Pasteur pipette and discard. Add 0·2 grammes of anhydrous sodium sulphate and inject 1 microlitre onto the G.L.C. column. Perform all injections in

duplicate. The chelate is stable for at least 30 minutes after which a slow decomposition occurs. While a sample is eluting from the chromatograph, perform the alkaline wash step on the next sample to be analysed and inject this after the chromium of the previous sample has eluted.

(C) Calibration

Prepare a blank digest by taking one unexposed Millipore filter through the relevant digestion procedure. Into each of four McCartney bottles pipette 1 ml of blank digest, and, with the Finnpipette, add 5, 10 and 15 microlitres of 10 micrognammes per ml beryllium standard solution to three bottles, respectively. Carry out the determination part of the procedure (B) from the addition of indicator and subtract the blank peak height from that given by each of the standards. The resulting figures should have a linear relationship. Once this has been established, it is only necessary to include a blank and one standard determination with each batch of samples tested. Calculate the amount of beryllium present by subtracting the blank peak height from that of the sample and comparing this figure with the corrected peak heights given by the standards.

Discussion

High volume air sampling equipment is installed at six selected sites in the Birmingham area and air drawn through Millipore filters pore size 0·8 micrometers (37 mm diameter) for weekly sampling periods at a rate to give a total air flow of about 200 cubic metres. This gives a detection limit of 0·0001 micrognammes of beryllium per cubic metre by the above method but this could be lowered if necessary by using larger filters and larger air flows. The detection limit for beryllium itself, obtained from numerous determinations by both digestion procedures is 1×10^{-12} g with the given instrument conditions but this could be lowered to 1×10^{-13} g by injecting larger volumes at decreased attenuation settings. This is possible since the major part of the blank value normally arises from the T.F.A. but, in the method described, it is reduced to a low level by the toluene distillation.

The use of toluene is preferred to the benzene favoured by other workers,[3,4,5] as, not only is it less toxic, but it also enables the T.F.A. (B. pt. approx. 105°C) to be purified by direct distillation with toluene (B. pt. approx. 110°C) as required. Thus none of the commerical T.F.A., an expensive reagent, is wasted.

The alkaline wash step performs two functions, removing from the organic phase both the indicator (a carboxylic acid) and excess T.F.A., the presence of the latter causing a characteristically high and unstable base line. The beryllium chelate is not stable for long periods in the presence of alkali but the deterioration can be retarded, or sometimes prevented, by removing the wash liquid prior to injection. The addition of anhydrous sodium sulphate to the wash liquid enables a clean and rapid separation of the two phases to take place after the manual shaking has been carried out.

Nitric acid and nitrous fumes interfere with the determination and they must be removed. This is accomplished by boiling the digested residues with 10 ml of water as indicated in the text and the use of, for example, ammonium oxalate,

was found to be unnecessary. The interference is due to the nitration of toluene during the determination step (B), which gives a large peak close to the beryllium chelate peak.

The perchloric acid digestion was found to be more convenient than that with sulphuric acid since the solution can be used to determine other metals by atomic absorption spectrophotometry without interference from sulphuric acid. No problems were encountered with its use in the method as detailed, although the alternative sulphuric acid digestion involves a less hazardous material where beryllium only is to be determined.

The sensitivity of the method is such that, for greatest accuracy, the standards and samples should be extracted at the same time. The speed, time and temperature of shaking is particularly important in this respect.

To test the precision of the method a set of combined precision and recovery determinations were carried out. These were done by adding 25 microlitres of a standard solution of beryllium (10 microgrammes per ml) to each of five clean Millipore filters contained in separate Kjeldahl flasks and carrying out the sulphuric acid digestion (A) and the determination (B) steps of the procedure on each one. At the same time 1 ml of blank digest solution, and 1 ml of blank digest solution containing 10 microlitres of a standard solution of beryllium (10 microgrammes per ml) were taken through the calibration (C) step of the procedure to provide a blank and standard for measurement purposes. The nominal amount of beryllium injected from each of the five precision determinations was thus 1×10^{-11} g and Table I shows the results obtained. All injections were carried out in duplicate and average peak heights calculated.

TABLE I

RECOVERY OF BERYLLIUM ADDED TO MILLIPORE FILTERS

Determination	Nominal amount of beryllium injected, 10^{-12} g	Beryllium recovered, 10^{-12} g
1	10	9·9
2	10	8·6
3	10	9·0
4	10	10·5
5	10	9·4

Blank value $\equiv 1 \times 10^{-12}$ grammes of beryllium
Average recovery = 95 per cent.
Relative standard deviation = 8 per cent.

Determinations carried out at the same level with the perchloric acid digestion, and also at the 1×10^{-10} g beryllium level with both digestion procedures gave similar or better results. Thus, overall precision and recovery are good.

Several other metals chelate with the reagent and for some, e.g. aluminium and chromium, reliable quantitative methods are available for estimation of trace amounts by this technique. Both these elements give peaks well separated from beryllium and they are reduced to non-interfering levels by the use of EDTA (contained in the buffer solution) in the cold. The elution times of Be, Al and Cr peaks under the given conditions are 1·2, 3·0 and 6·0 minutes, respectively.

The results of several hundred analyses carried out so far are presented in Table II.

TABLE II

SUMMARY OF RESULTS FOR BERYLLIUM IN AIR PARTICULATES

Site no.	No. of filters analysed	Type of site	Results above detection limit	Range of results *Micrograms of Be/metre*^{3}	Average
5	82	Monitoring non-ferrous metal company mentioned in Introduction	26	<0·0001–0·0009	0·00026
8	86	Monitoring non-ferrous metal company mentioned in Introduction	37	<0·0001–0·0015	0·00031
9	81	Monitoring non-ferrous metal company mentioned in Introduction	26	<0·0001–0·0013	0·00031
13	86	Residential site control	20	<0·0001–0·0009	0·00029
15	70	Residential industrial area	18	<0·0001–0·0012	0·00029
16	82	Fringe of urban area close to airport	25	<0·0001–0·0006	0·00027

The sites referred to in Table II represent a variety of industrial-urban locations in the Birmingham area of which site no. 8 is situated near to, and downwind of, a beryllium processing plant. Filters from this site show the greatest number of positive results as well as the highest concentrations of beryllium recorded, though the average figure is not significantly higher than that of some other sites. The overall results demonstrate that, in relation to the Threshold Limit Value mentioned earlier, negligible amounts of beryllium occur in the atmosphere of the Birmingham region.

Conclusion

The G.C. determination of beryllium by chelation with trifluoroacetylacetone is a reliable method, with excellent sensitivity and specificity, for the estimation of trace quantities of the metal in air particulates.

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A Rapid G.L.C. Method for the Determination of Benzoic Acid in Soft Drinks and Similar Products

M. E. NEALE

Barnett & Foster Ltd., Wellingborough, Northants

AND

J. RIDLINGTON

International Flavours and Fragrances Ltd., Haverhill, Suffolk

A rapid G.L.C. procedure is presented which eliminates the need for special reagents, has a total analysis time of less than 20 minutes and should be adaptable to the determination of sorbic acid and to the esters of *p*-hydroxy benzoic acid.

The use and control of benzoic acid and other permitted preservatives has been adequately reported in the comprehensive paper by Fogden *et al.*[1]

The following method was originally developed by one of the authors (J.R.) for the determination of benzoic acid in blends of fruit and sugar syrup, and with modification, has been found to be suitable also for use with soft drinks of the squash and carbonated beverage type and with concentrated citrus and soft fruit juices.

APPARATUS

Pye Gas Chromatograph Series 104 (or equivalent).
Gallenkamp Centrifuge to take 50 ml tubes (or equivalent).
Laboratory flask-shaker (preferred, but optional).

REAGENTS

1. *Chloroform A.R.*
2. *Acid-brine:* Mix 750 ml of saturated sodium chloride solution with 100 ml of concentrated hydrochloric acid and dilute to 1 litre with water.
3. *Standard Component Solution:* Dissolve about 0·35 g, accurately weighed, of sodium benzoate of known purity (*P* per cent.) in sufficient water to give 500 ml of solution.
4. *Internal Standard Solution*: Dissolve 1·0 $\pm$ 0·1 g of phenylacetic acid (or 0·6 $\pm$ 0·05 g of *para*toluic acid) in 10 ml of M NaOH and dilute to 100 ml with water.

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GAS CHROMATOGRAPH CONDITIONS

Column	Glass, 1·5 m × 4 mm i.d.
Packing	1 per cent. DEGS-PS (Supelco Inc.) on 80–100 mesh Chromosorb W.HP.
Oven temperature	175°C (isothermal).
Injection temperature	175°C.
Detector	Flame ionisation.
Carrier gas	Oxygen-free nitrogen, 45 ml/min.
Hydrogen	50 ml/min.
Air	300 ml/min.
Attenuation	10 × 10^2 (if integrator not used).
Chart speed	10 mm/min.
Integrator	Pye-Unicam DP-80 (or equivalent, optional).
Time for run	4 minutes for benzoic acid analysis; 15 minutes for propyl *para*-hydroxy benzoate.

METHOD

Accurately weigh m grammes of sample (where m = 6000/expected mg/kg of benzoic acid) into a 100 ml screw-cap jar. Add 1·0 ml of internal standard solution, 15 ml of acid brine and 2·5 ml of chloroform. Shake vigorously for 2 minutes. Transfer to a centrifuge tube and spin for 5 minutes at about 2000 r.p.m. Inject 1·0 μl of the chloroform extract into the gas chromatograph using the conditions given. Concurrently prepare and inject a standard mixture, prepared by replacing the sample by 10·0 ml of standard component solution.

Calculate the benzoic acid content:

$$= 10{,}000 \times \frac{h_3}{h_4} \times \frac{B}{m} \text{ milligrammes per kilogramme}$$

thus $$10{,}000 \times \frac{h_3}{h_4} \times \frac{h_1}{h_2} \times \frac{1}{K} \text{ mg/kg}$$

where $$K = \frac{\text{mass of phenylacetic acid in standard mixture (grammes)}}{\text{mass of benzoic acid in standard mixture (grammes)}}$$

$$= \frac{1{\cdot}0}{100} \times m_1 \times \frac{10}{500} \times \frac{P}{100} \times \frac{122{\cdot}1}{144{\cdot}1} = \frac{Pm_1}{59{\cdot}01},$$

h_1 = height or area of phenylacetic acid peak on standard mixture chromatogram,

h_2 = height or area of benzoic acid peak on standard mixture chromatogram,

h_3 = height or area of phenylacetic acid peak on sample mixture chromatogram,

h_4 = height or area of benzoic acid peak on sample mixture chromatogram,

P = percentage purity of sodium benzoate used,

m_1 = mass in grammes of sodium benzoate used to prepare the standard component solution,

m = mass in grammes of sample.

Notes

1. The standard mixture may be kept for one week in a stoppered container, and used daily to calculate the response factor.
2. When analysing viscous samples, it is advisable to add a small volume of water to increase the extraction efficiency.

Results

Extraction efficiency experiments were carried out to determine the shaking time required to effect maximum removal of benzoic acid using viscous samples of blends of fruit and sugar syrup (this would ensure that the time selected for this type of product would also be suitable for less viscous liquids). The results in Table I show a shaking time of 2 minutes to be adequate.

TABLE I

EXTRACTION TIMES OF BENZOIC ACID

Shaking time, *minutes*	Benzoic acid, *mg/kg*
0·5	622
1	676
2	676
4	693
8	687

Recovery experiments were performed on orange squash, carbonated cola and a concentrated brewed ginger beer compound. The results are shown in Table II, in which the column headed "Found—original" gives the total found less that originally present in the samples.

TABLE II

RECOVERIES OF BENZOIC ACID

Product	Benzoic acid added, *mg/kg*	Benzoic acid found, *mg/kg*	Recovery, *per cent.*
Orange squash	172	165	96·0
Carbonated cola	58	59	101·7
Ginger beer compound	356	347	97·5

This method has also been compared, using the ginger beer compound, with the Association of Official Analytical Chemists extraction method,[2] a steam distillation and u.v. measurement procedure[3] and a method using H.P.L.C.[4] The results are given in Table III. A statistical analysis of the results shows that when the AOAC, H.P.L.C. and u.v. methods are compared with the G.L.C. method, the respective differences between the means are not statistically significant.

TABLE III

COMPARISON OF THE DETERMINATION OF BENZOIC ACID IN SOFT DRINKS BY VARIOUS METHODS

Sample	GLC, *mg/kg*	AOAC, *mg/kg*	HPLC, *mg/kg*	u.v., *mg/kg*
1	2051	2284	2151	1993
2	2116	2218	2113	2201
3	1793	1935	1862	1896
4	2266	2322	2516	2104
5	2173	2201	2316	2160
6	2010	2045	2093	2101
7	1801	1740	1960	1886
8	1708	1793	1814	1891
8	2078	2100	2096	2200
10	1757	1862	1900	1980
Mean	1975	2050	2082	2041
Standard deviation	195	209	215	127

Discussion

In soft drinks, benzoic acid is the only preservative of note relevant to this communication, but it has also been found that sorbic acid and the methyl and *n*-propyl esters of parahydroxybenzoic acid (parabens) are extracted under the conditions given above, and it is suggested that the method would be equally

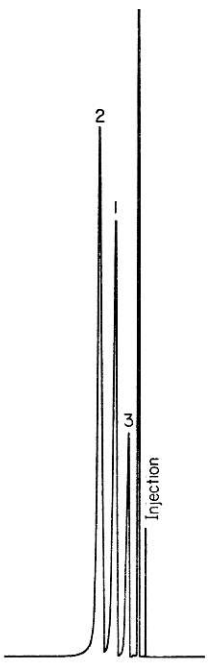

Fig. 1. A typical benzoic acid chromatogram. 1, Benzoic acid; 2, phenylacetic acid; 3, sorbic acid.

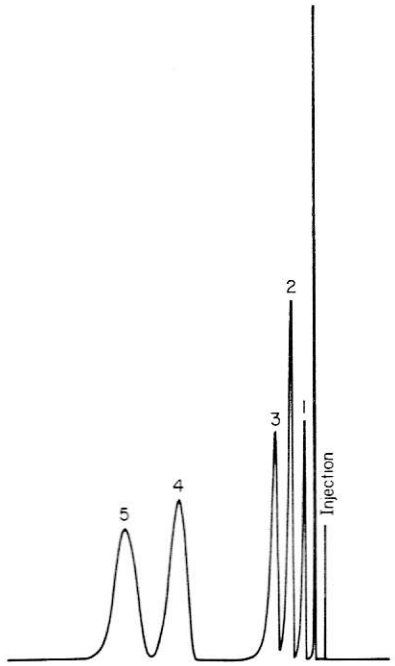

Fig. 2. Relative elution times of four preservatives. 1, Sorbic acid; 2, benzoic acid; 3, phenylacetic acid; 4, methyl *p*-hydroxybenzoate; 5, *n*-propyl *p*-hydroxybenzoate. (Phenylacetic acid is the internal standard.)

suitable for these preservatives, using an appropriate extraction method for the sample type being analysed. Figures 1 and 2 show a typical benzoic acid analysis chromatogram and the relative elution times of five preservatives. Of interfering chemicals, only 3,4-dihydrocoumarin has been found to co-elute with benzoic acid, but this may be removed by a preliminary extraction from an alkaline medium. Although not commonly found in soft drinks, vanillin and ethyl vanillin (the latter eluting first) elute close to phenylacetic acid, and an alternative internal standard (*para*-toluic acid) may be used. However, because of its availability in the soft drinks and flavours industries, phenylacetic acid has been chosen as the usual internal standard (a statistical experiment showed no significant difference between the means when *para*-toluic acid was compared with phenylacetic acid).

Conclusion

The method described above has been in operation in the quality control laboratories of Barnett & Foster Ltd. for the past 9 months for the routine determination of benzoic acid in soft drinks, concentrated soft drink compounds and concentrated citrus and soft fruit juices. The G.L.C. column initially prepared is still in use.

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Letter to the Editor

Some Recent Public Analysts

Sir,

In *The First Fifty Years of the Society of Public Analysts* by Dyer and Mitchell there were outlined the principal papers published by members during the five decades of the period 1875 to 1925. Since then a former Government Chemist[1] and two former Public Analysts[2,3] have made their own contributions, whilst in the recent publication *The Practising Chemists,* Chirnside and Hamence have re-outlined analytical history as well as noting some of the advances made by their colleagues since 1925. Nevertheless, many gaps remain to be filled, much work carried out from 1930 onwards by a number of Public Analysts having been left unrecorded, though reference has been made elsewhere to one important investigation, viz. the 1934 results of the determination by Elsdon and Stubbs[4] of the freezing points of 1,000 samples of milk by the Hortvet method, which originated in the U.S.A. and served within a comparatively narrow range to distinguish between watered milks and those naturally low in non-fatty solids.

Meantime, the composition and properties of malt vinegar and its synthetic imitations had continued to attract attention, the ash, nitrogen and phosphorus contents of the former being markedly greater than those in the so-called artificial variety, later to be known as "non-brewed condiment". Then in 1938 a notable advance was made through the introduction of the "Acid Oxidation Value" by a Westminster City Analyst, F. W. Edwards, and his assistant Nanji,[5] this with the accompanying iodine and ester values enabling differences of other kinds to be drawn between the two types already mentioned as well as between other types, this welcome advance being subsequently extended by Lyne and McLachlan[6] in their "Alkaline Oxidation Value" method of 1946 from their London laboratories.

During this period Arnold Tankard, the Kingston-on-Hull City Analyst, had retired and been succeeded by his deputy, Douglas Bagnall, who now became the opposite number of his namesake, Howard Bagnall, the Birmingham City Analyst. Douglas Bagnall, during the Second World War, was responsible for two publications of note, the first of these (in 1942)[7] providing useful information regarding the composition of various brands of commercial cocoa, for which there had never been any legal standard. It was therefore desirable to learn what could reasonably be regarded as the normal average percentages of moisture, fat and fibre in cocoa, especially that sold under wartime conditions. The second paper[8] dealt with the determination of the percentage of dried egg in fruit curd, a necessarily lengthy process to which a fully satisfactory alternative has yet to be found. A much shorter method

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for the determination of dried egg present in admixture with various flours[9] had, however, gradually become available, as had also one which made possible, in a direct run-through apparatus, the rapid extraction of fat from powders containing it in at least half the time taken by the long-serving Soxhlet apparatus, the time in the case of cocoa being reduced to one twelfth (2 hours instead of 24).[10]

Tankard lived to see Bagnall himself retire and take up sketching as a pastime on the Yorkshire moors above Pickering. Before this happened, however, Bagnall would almost certainly have worked with a much smaller quantity than 20 grammes when analysing a sample of lemon curd (for the estimation of egg content), for by that time the colorimetric molybdenum blue method for the determination of phosphorous[11] had become available and applicable, moreover, through the phosphorus pentoxide figure, for the assessment of the percentage of fruit juices in soft drinks.

Now, just as George Elsdon had given us the lead in 1930 over the Hortvet apparatus, Richard Sutton (at Derby) felt that Public Analysts must devise means for the determination of Vitamins A and D in margarine if they were not to see others carrying out the work. The result of the acceptance of this challenge was the ultimate introduction of the spectrometric and spectrophotometric instruments with which we are today so well familar. Much later, in 1964, thanks to a neat method devised by the two Singapore analysts, Kum Tutt and Leong,[12] the determination without difficulty of Vitamin C in blackcurrant and other highly coloured syrups was made possible, the method depending upon the reduction of mercuric chloride to calomel in presence of acetone.

Meantime, in Liverpool's extensive and well equipped City Laboratory, W. H. Roberts had been succeeded by J. F. Clark, and G. H. Walker, one of Roberts' staff, had gone first to Salford and then to Lancashire. W. Gordon Carey[13] in Newcastle had established himself as an authority on water supply, and Joseph Markland, following Stock's resignation, had been appointed the first full-time Durham County Analyst, later succeeding Sutton in Matlock as Derby County Analyst. F. C. Bullock, Leicester County Analyst and a Past President of the A.P.A. (formed in 1953) was better known for the humorous passages in his Annual Reports than for any published research work. His deputy, E. R. Pike, subsequently succeeded him. E. G. Whittle, originally from Portsmouth, where he had worked with R. P. Page, acted as deputy for a while to E. T. Illing (County of Somerset) with whom he collaborated in modifying Edwards and Nanji's method[14] and in devising a method for the determination of soya in wartime sausages,[15] Whittle later moving to Bristol in the footsteps of Edward Russell and F. E. Needs, and, at Canynge Hall, gathering round himself a body of first-rate analysts, several of whom, led by David Taylor, proved their worth as producers of many original papers. Whittle, Albert Houlbrooke, G. V. James and R. A. Dalley, who succeeded his former chief, Manley, at Leeds, all attained the rank of Major in various branches of the Armed Forces dealing with Public Health work. Houlbrooke and co-workers[16] from the Staffordshire County Laboratory subsequently published useful figures for the constituents of ground almonds, cashew nuts

and peanuts; A. N. Leather,[17] a former member of the staff of F. W. Richardson, for his part devised an alternative method for the determination of benzoate preservative, and moved to Salford and eventually reverted to Manchester, where at one time he had been deputy to Harri Heap. Leather's successor, J. B. Aldred, now functions in one of several purpose-built laboratories, a similar one having been already erected in Portsmouth. The corresponding Lancashire and Somerset Laboratories, at Preston and Taunton respectively, form part of the County Council Offices. The Portsmouth ones are described as "Project 3112" in Audrey Cooke's *Public Analysts of Portsmouth*, 1872–1972. In London, Eric Voelcker had been carrying on a family practice which, apart from foods and drugs, had devoted special attention to agricultural problems. In Wales, L. E. Coles became Glamorgan County Analyst and A. R. Phillips the Cardiff City Analyst, an appointment once held by Stanley Dixon, son-in-law of the late John White of Derby County, whose proud boast it was that no case arising out of a sample certified by him had ever been lost; at Carmarthen, D. C. Jenkins continued his county work along with a private practice following in Herbert Evans' footsteps. Further, in Exeter "Admiral" Thomas Tickle, has been succeeded first by C. V. Reynolds and then his son, E. B. Reynolds. By this time, moreover, the Public Analyst had come to be regarded also as Scientific Adviser and in several instances had been accorded this title. The problems presented to the Public Analyst have always been varied, but never more so than now, and, whilst the basic principles remain and have still to be applied, the men in charge today are having to bear a burden of much greater responsibility than did those of us who were in office twenty years ago.

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C. H. MANLEY
Bristol

Announcement

The following resolution was accepted at the Annual General Meeting of the Association of Public Analysts on Saturday, 6 May, 1978.

Re-formed Meat

"The Association of Public Analysts, whilst anxious not to restrict developments in food technology, has a duty to safeguard the traditional descriptions of food products.

"In particular, it is the opinion of the Association that if 're-formed meat' is used in the preparation of a food product, that product must not be described by a name (such as 'steak pie', 'sliced pork') that implies the presence of a cut of meat.

"In this context, 're-formed meat' means meat that has been disintegrated by grinding or similar treatment and subsequently processed with or without the addition of minor processing aids, so as to give the impression of intact pieces or slices of meat."