

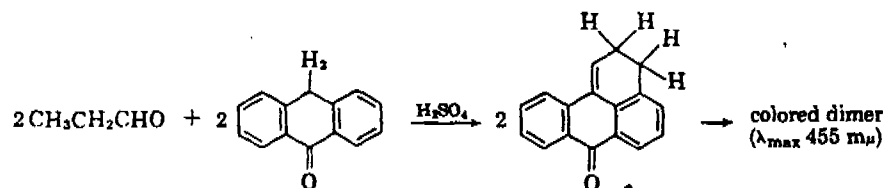
The violet-red color of the dibenzanthrone may be stabilized by interaction with the H_2SO_4 . It may be hypothesized that HSO_4^- and H_2SO_4^+ contribute π electrons to the dibenzanthrone.

Crotonaldehyde reacts by a similar mechanism (2, 9). By condensation of crotonaldehyde with anthrone, 11-methyl-benzanthrone is obtained (9), and dimerization may be assumed to follow.

To test the proposed mechanism, benzanthrone (Calbiochem, Los Angeles 63, Calif.) was dissolved in concentrated

and crotonaldehyde (Table I). Evidently the condensation of these compounds with anthrone to give benzanthrone (or its methyl derivative) is stoichiometric and goes to completion under the test conditions.

The deviation in the spectral data for the propionaldehyde-anthrone complex from that of other saturated aldehydes may be explained on the assumption that propionaldehyde forms a cyclic compound similar to that of malonaldehyde, except that the 12 and 13 positions in benzanthrone are saturated.



sulfuric acid and further diluted to give suitable concentrations in a sulfuric acid-water mixture identical with that used in the anthrone test. The molar absorptivity of this solution at the λ_{max} of 510 $\text{m}\mu$ was 7.8×10^3 , very close to the values found for the anthrone reaction products with malonaldehyde, acrolein

Other saturated aldehydes probably condense with anthrone without cyclization. The structures of the resulting pigments are not known, nor is there evidence on which to base an explanation of the differences noted in the activity of formaldehyde as compared to other saturated aldehydes.

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Determination of Toxic Organic Compounds in Admixture in the Atmosphere by Gas Chromatography

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► A variety of chemical and physical methods exists for detecting toxic organic compounds when present alone in the atmosphere, but these often prove inadequate when two or more contaminants are present in admixture. Gas chromatographic methods described so far—e.g. for air pollutants in "smog"—have, in general, required the use of special cooled traps and have involved lengthy sampling periods. In this paper, a method is described which traps the components on a solid absorbent at room temperature and which requires only a relatively small sample of air; the total time for a test, including the sampling stage, is thus only 10 to 15 minutes. It has been applied, for example, to atmospheres near a chlorination plant where toluene, benzyl chloride, benzal chloride, benzotrichloride, benzoyl chloride, and benzaldehyde might be encountered. Because the procedure is so simple and rapid, it has also been used for

detecting single components such as nitrobenzene. It is deduced that the method would be applicable to the majority of organic compounds in the list issued by the American Conference of Governmental Industrial Hygienists.

TO ENSURE the safety of industrial personnel who might be exposed to toxic compounds in the atmosphere, threshold limit values have been recommended by the American Conference of Governmental Industrial Hygienists (17) and these values have been adopted as maximum permissible concentrations in Great Britain by the Ministry of Labour (18). A considerable number of chemical methods has been developed for various likely contaminants—e.g., (16)—and these have been applied for many years; examples are the determination of nitrobenzene, of aniline and other arylamines, of tolylene diisocyanate, of formaldehyde, and of

chlorinated hydrocarbons. These methods usually involve bubbling the atmosphere through a suitable absorption solution and development of an appropriate color. They are often specific for a certain compound (or at least for a class of compounds) but each test involves quite a lot of work and requires a fairly large sample of air, with a correspondingly lengthy sampling period. More recently dry absorber tubes have been developed—e.g., by Drägerwerk, Moislinger Allee 53/55, Lübeck, W. Germany—which indicate how much of an expected contaminant is present according to the length of stain seen in the tube after drawing air through for the required time, but these tubes have so far been applied mainly to inorganic gases such as phosgene and carbon monoxide and to a few common volatile organic compounds.

The detection of a single component in the atmosphere will, however, be inadequate whenever there is a possibility

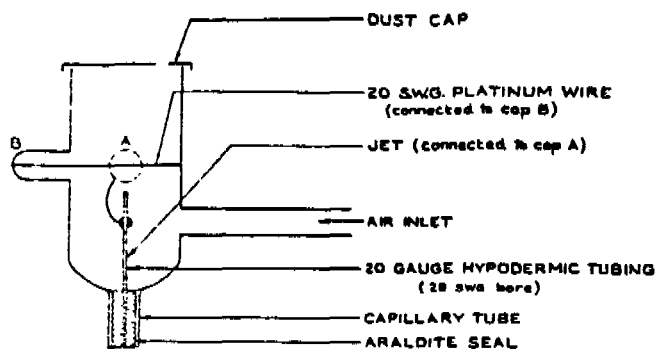


Figure 1. Flame ionization detector

that several toxic compounds may be present; in such circumstances it is desirable that a single test should indicate which of the likely contaminants is present, and give their approximate concentrations. Gas chromatography offers the best means of achieving this, but so far no publication has appeared describing a simple and rapid procedure suitable for industrial application. This paper describes such a procedure.

Gas chromatography has been applied to studies on the nature of contaminants in the atmosphere arising as a result of smog and the running of automobile engines. This work (6, 7, 19) has generally involved the sampling of large volumes of air, the removal of atmospheric water with drying agents (which may interfere by retaining some of the components), the isolation of the components in cooled traps containing a solid adsorbent—e.g., activated charcoal—or a conventional GLC packing, and the use of a thermal conductivity cell as detector. The use of the flame ionization detector, with its very high sensitivity to organic compounds and its insensitivity to air and water, enables samples of the contaminated atmosphere to be taken in a gas sampling bulb and injected directly by means of a hypodermic syringe (8), but we have found that this procedure may result in losses, particularly with higher-boiling compounds. We prefer, therefore, to sample the atmosphere by drawing a small volume through a short, straight absorption tube at room temperature packed with a suitable GLC filling or silica gel; this tube is then attached to a GLC column and the organic compound(s) are desorbed by electrical heating (2) and detected in the usual way. Special apparatus such as gas bulbs, drying tubes, and cooling traps are thus replaced by absorption tubes which are easily portable and are immediately ready, after desorption, for using again without repacking. This procedure, which could readily be

adapted in an automatic apparatus, is specifically designed as a rapid and convenient means of checking that atmospheric conditions are safe.

APPARATUS AND MATERIALS

Chromatographic Unit. Any gas chromatograph with a flame ionization detector could be adapted for use in the way described below. Our apparatus was adapted from that developed for general analytical work by A. Heywood (to whom grateful acknowledgment is made), based on the original detector described in

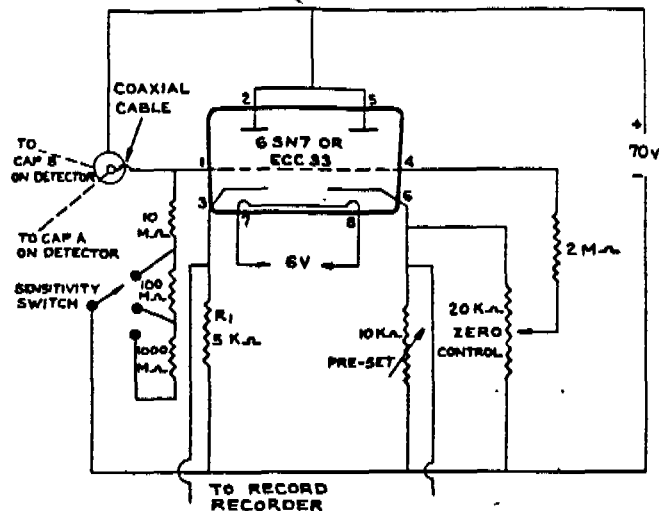


Figure 2. Cathode follower circuit

British Patent 838189 (3-5). The essential parts of this apparatus are:

CHROMATOGRAPHIC COLUMN. The folded 3-foot $\times$ 4-mm. bore glass chromatographic column has four 9-inch limbs, one of them (the inlet) protruding 0.5 inch longer than the other end (the exit); there is no special assembly on the inlet end of the column. It is inserted into a 12-inch $\times$ 2-inch i. d. electrical heater.

FLAME IONIZATION DETECTOR (Figure 1). This consists of a glass bowl with a 1.5 inch length of 20 gauge stainless steel tubing (ground square at each end) sealed into the 2-mm. bore

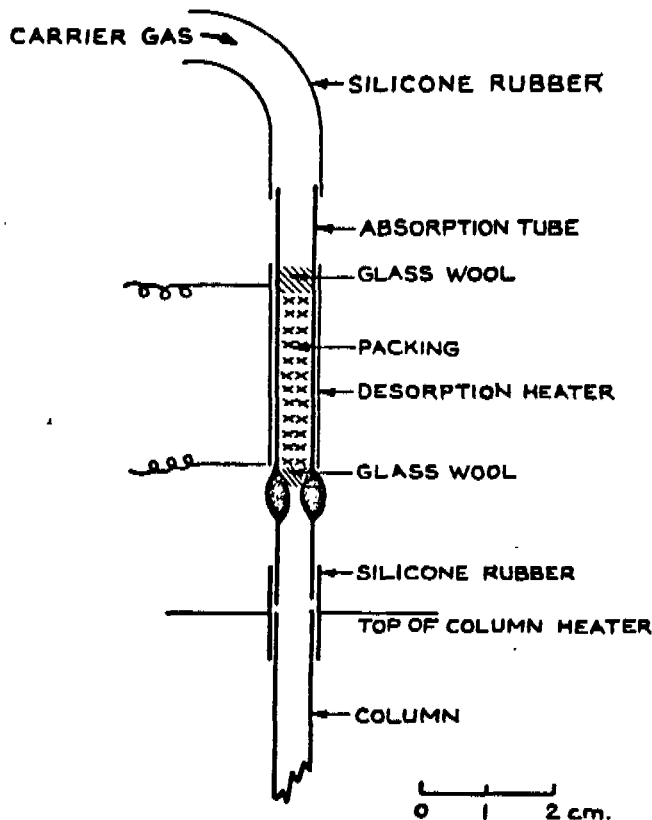


Figure 3. Absorption tube and desorption heater in position on top of column

capillary tubing fused at the bottom of the bowl. Thin copper wire is soldered to this stainless steel jet, which forms one electrode; the second electrode is a piece of 20-gauge platinum wire sealed at 5 to 7 mm. above the jet. The glass capillary tube is connected to the exit from the chromatograph column by silicone rubber tubing.

CATHODE FOLLOWER CIRCUIT AND RECORDER. This is the single valve circuit of Figure 2, used with a recording galvanometer (Record Electrical Co. Ltd., Altrincham, Cheshire, England) with internal resistance of 1500 ohms, 0.3-ma. full scale deflection, chart speeds of 3 inches and 12 inches per hour. The sensitivity switch gives full sensitivity when set at 1000 megohms and, respectively, $1/10$ and $1/100$ sensitivities when set at 100 megohms and 10 megohms. If a potentiometer recorder is used instead, a suitable attenuating circuit is added.

The accessories required for use with the chromatographic unit are as follows:

Absorption Tubes. These are glass tubes 2.5 inches long, 4.5-mm. bore, with a bulged constriction in the exit end (Figure 3). Each contains a 1-inch length of suitable packing, held in position by glass or quartz wool plugs, and packed so that the impedance is 4 to 5 cm. Hg at 100-ml.-per-minute air flow. With the 100- to 200-mesh silica gel packing very little or no compression will be necessary, but with the 100- to 120-mesh Celite stationary phase packings the final 1-inch length at the above impedance is obtained by filling a 1.5-inch length of the tube by tapping, and then compressing by ramming with a glass rod, withdrawing or adding more packing as necessary. They are stored in glass-stoppered test tubes and can be used repeatedly without repacking.

Desorption Heater. This is a copper foil tube 1.25 inches long and 7-mm. bore, insulated with asbestos tape and wound with resistance wire to give 12 watts; this fits snugly over the absorption tube so that it rests on the bulged portion (Figure 3). When in use it is connected in series with a variable resistance—e.g., 0 to 10 ohms.

Sampling Apparatus. Most of the conventional units can be used for drawing the atmosphere through an absorption tube—e.g., a vacuum line and flowmeter, a D.S.I.R. hand pump (16), a rubber-bulb hand pump (9) or a hypodermic syringe of approximately 5- to 100-ml. capacity. A gas sampling bulb, with one or two taps and with volume equal to the volume of sample desired, can also be used by evacuating it, connecting it to an absorption tube and opening the tap between the absorption tube and the bulb. The sampling time under these conditions is 1 to $1\frac{1}{2}$ minutes. If an integrated sample over a longer time is required, a capillary tube of suitable dimensions is inserted between the absorption tube and the bulb; thus, a 7.5-inch length of 0.015-inch bore capillary tubing increases the sampling time to 3 to 4 minutes.

The rate and duration of sampling depend on the particular test in hand;

Volume of 100 to 500 ml., sampled during 1 to 2 minutes, is usually suitable.

Column Packings. Celite 545 (Johns-Manville Corp.), graded to 30- to 60-mesh B.S.S., heated at 100° C. with concentrated hydrochloric acid for several hours, washed, dried at 300° C., and again graded to 30- to 60-mesh B.S.S., is used with these stationary phases, in the stated proportions:

- 7:3 Silicone Elastomer E.301 (ex I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire, Scotland).
- 9:1 Poly(ethylene glycol adipate), m.p. about 50° C., mol. wt. about 1200.
- 9:1 Octadecylamine-ethylene oxide condensate (mol. wt. 1000).
- 9:1 Polyethylene glycol 400.
- 4:1 Adiponitrile.

After packing, the columns are pretreated to remove volatile components by heating for several hours in a stream of nitrogen (50 to 100 ml. per minute) at the appropriate temperature—i.e., 320°, 180°, 180°, and 110° C., respectively, for the first 4 phases listed above; adiponitrile is used only at room temperature and requires no pretreatment.

Absorption Tube Packings. Celite 545 (Johns-Manville Corp.), graded to 100- to 120-mesh B.S.S., heated at 100° C. with concentrated hydrochloric acid for several hours, washed, dried at 300° C., and again graded to 100- to 120-mesh B.S.S., is used with the following stationary phases in the proportions 7:3

Silicone Elastomer E.301.
Polyethylene glycol 400.

These packings are pretreated in bulk—i.e., before filling the absorption tube—by heating for several hours in a stream of nitrogen (50 to 100 ml. per minute) at, respectively, 320° and 110° C. to remove volatile components.

Silica gel, Davison (U. S. A.) grade 923 (100- to 200-mesh). This is pretreated—i.e., freed from adsorbed impurities—after filling the absorption tubes by carrying out repeated blank tests (see below—usually 2 to 3 suffice) until the impurity peaks seen after each 2-minute desorption heating period finally disappear; a convenient GLC column for following the pretreatment is that containing Silicone Elastomer E. 301 at 120° C.

PROCEDURE

Assembly and Testing of the Apparatus. The outlet end of an absorption tube, containing the required packing, is connected to the inlet of the chromatographic column (at the required temperature) by silicone rubber tubing. The desorption heater is placed in position so that it rests on the bulging constricted portion of the absorption tube, and the inlet end of the absorption tube is connected to the carrier gas supply (1:1 H₂/N₂ at 50 ml. per minute) with silicone rubber tubing (Figure 3). A gap of about 1 cm. is maintained between the silicone rubber tubing at each end of the absorption tube and the desorption heater.

When the apparatus at full sensitivity, the desorption heater is switched on for 2 minutes at 12 watts—i.e., with the variable series resistance at 0 ohms; the baseline is observed for 15 minutes and if straight (or containing only very minor peaks), the apparatus is considered ready for use. If the baseline is not straight and/or peaks are present, and if this condition persists after several desorption cycles, it probably indicates that the desorption heating is causing some volatilization from the absorption tube packing; this is eliminated by keeping the heating period constant at 2 minutes and reducing the wattage by adjusting the variable series resistance until the resulting baseline is satisfactory (this step will be more necessary with the polyethylene glycol packing than with the silicone, because of the greater thermal instability of the former). The reduced wattage is noted and used subsequently, after ensuring that it is still sufficient to desorb the compounds being determined.

If reduction in the wattage does not give a satisfactory baseline, the cause is probably due to

(a) the trapping of volatiles from the carrier gas line by the absorption tube, with subsequent release on desorption. This may be significant if there are appreciable lengths of rubber and/or plastic tubing in the line, and may be corrected by minimizing the length of such tubing in the line, making it as far as possible in glass or metal tubing, with butt joints.

(b) thermal instability of the silicone rubber joints. This should be unlikely if approximately 1-cm. gaps are maintained between the heater and the rubber at each end of the absorption tube. If necessary, a fresh piece of silicone rubber should be used which has been preheated for several hours at a temperature which does not cause it to go brittle (approximately 250° C.), and/or the gaps between the heater and the rubber should be increased.

Calibration Test. The carrier gas supply line is detached and the stipulated volume (usually 0.02 ml.) of a standard solution (usually in CS₂) of the expected toxic compound(s) is introduced on to the glass or quartz wool plug at the inlet of the absorption tube, using a micropipet or a hypodermic syringe; the carrier gas supply line is reconnected, the flow restarted, the detector flame lit, and the desorption heater switched on for 2 minutes. The slight signal due to the elution of the CS₂ solvent is ignored. During the next 15 minutes, the expected compound(s) are eluted in peaks approximately $1/10$ to $1/4$ of full scale deflection; no other peaks should be apparent. The peak areas and retention times are noted.

Collection of Sample. The requisite volume of the atmosphere to be tested is drawn through an absorption tube in the direction of flow from inlet end to outlet end (see Sampling Apparatus). When an

average concentration over a longer period of time. When a mixture is measured, the area of elution is measured, and the loss is corrected accordingly. When the D.S.I.R. pump is used, at least 0.5 minute must be allowed for each stroke, with 10 seconds between each stroke, and the piston must be held during this 10-second interval so that the partial vacuum in the barrel does not suck it forward and result in a low sample volume. After sampling, each absorption tube is placed in its stoppered test tube, and is usually tested as soon as possible afterwards.

Testing the Sample and Assessing the Results. The absorption tube is connected to the GLC apparatus at the required temperature as described above, the desorption heater is switched on for 2 minutes, and the carrier gas flow is started after the first minute. The record is then observed to see whether any peaks are present at the expected retention times.

Since the volume of calibration solution and the volume of air sample are fixed (and specified) in each particular case so that each peak corresponds to a threshold limit value, it is usually sufficient to rely solely on visual inspection of the records for the test and the calibration to decide whether the atmosphere contained less or more than the limit for each component. When numerical results are required, the areas under the peaks in the calibration records are measured and the mean for each peak (A_c) is calculated; the areas under the peaks in the test record (A_T) are also measured. If for a given component $L_{p.p.m.}$ (v./v.) is the threshold limit value represented by the calibration peak, then

Concentration in sample

$$\text{under test} = \frac{LA_T}{A_c} \text{ p.p.m.}$$

If the result is required in milligrams per cubic meter at 25° C., the result in parts per million is multiplied by $M/24$, where M is the molecular weight of the compound.

THEORY

The maximum permissible sample volume for quantitative retention of a compound by an absorption tube containing a GLC packing could be related to the breakthrough volume curve, determined by carrying out a frontal analysis experiment in which a fixed flow of an atmosphere containing the compound is passed through the tube connected to a GLC detector. However, it was considered simpler to relate the maximum permissible sample volume to the readily determinable retention volume of the compound on the tube in the following manner.

Consider a sample volume V_s equal to the retention volume V_R , and let both equal 100 arbitrary units. It is clear that the compound will not be retained quantitatively on the tube,

Table I. Retention Volume Data Using 1-inch Celite/Silicone Adsorption Tube at Room Temperature

	B.P., ° C.	V_R (retention volume, ml.)
Benzene	80	29
Cyclohexane	81	26
Toluene	110	77
Pyridine	115	110
n-Butanol	118	36
p-Xylene	138	210
Cyclohexanone	155	230
Cyclohexanol	162	230
Benzaldehyde	179	330
Benzyl chloride	179	590
Aniline	184	580
Benzoyl chloride	197	1100
Benzal chloride	207	2100
Nitrobenzene	210	1200
Benzotrichloride	214	5800

since the peak maximum corresponding to the first unit will have reached the end of the tube, and thus the compound in this first unit will be only 50% retained on the tube; this percentage will, however, increase for the successive units until a unit is reached, corresponding to the breakthrough volume, which is just retained 100% on the tube; all succeeding units until the 100th will be also 100% retained. The distribution of each unit will approximate to a Gaussian type towards the outlet end of the tube (which is the portion of interest) of standard deviation $\sigma = V_R/\sqrt{n}$, where n is the number of theoretical plates in the tube. Consider the distribution of the i th unit of sample volume; the extent to which this is not retained on the tube is given by that fraction of the area under the curve of the probability integral outside the bounds of the tube—i.e., $0.5 - 1/\sqrt{2\pi} \int_0^t \exp(-t^2/2) dt$, and the percentage of the total sample not retained on the tube is therefore

$$i = 100 \sum_{i=0}^{\infty} [0.5 - 1/\sqrt{2\pi} \int_0^t \exp(-t^2/2) dt],$$

where $t = i/\sigma$

Since a typical value of n is 32, σ is 17.5, and the above expression is calculated with the aid of a table of the probability integral to be 7%—i.e., if the sample volume is equal to the retention volume, 93% will be retained by the tube. Most of the loss is from the initial portion of the sample volume; thus if the sample volumes are reduced to 90% and 80% of the retention volume, then the losses are reduced to 3% and 1%, respectively. Similar figures were obtained by graphical integration of the breakthrough curve derived from Glueckauf's treatment (11). It seems appropriate therefore to stipulate a

maximum permissible sample volume $V_s^{\max} = 0.8 V_R$; this will ensure that the sampling efficiency is 99%.

RESULTS

Preliminary Experiments. A 1-inch length of Celite/silicone packing in the absorption tube was examined to see if it behaved as predicted theoretically in the extent to which it retained compounds at room temperature. Silicone Elastomer E.301 was chosen because it was considered least likely to give rise to volatile impurities which would affect the baseline.

Values of V_R (and thus of $V_s^{\max}$) can be calculated from the specific retention volume, V_s , by means of the simplified expression:

$$V_R = V_s TW_L/273 \quad (1)$$

where T is the temperature of the tube (say 298° K.) and W_L is the weight of stationary phase in the tube (0.060 gram); the pressure gradient correction factor, j , has been taken as unity and the gas hold-up, V_M , is negligible (15). Only few values of V_s are given in the literature, especially at room temperature, but substitution of extrapolated V_s values for benzene, toluene, and p-xylene (12) in the above equation gave V_R values of 37, 97, and 220 ml. These were compared with values determined experimentally by connecting the absorption tube at room temperature directly to a flame ionization detector, loading a dilute CS₂ solution of benzene, toluene, and p-xylene, and passing carrier gas (1:1 H₂/N₂) at 50 ml. per minute; the retention volumes were 29, 77, and 210 ml., in satisfactory agreement with the above values, especially in view of the extrapolation and the fact that the V_s values given are for Silicone 702. Hence, while a 5-ml. sample of air drawn through the tube should give good recovery for all three compounds (since V_R is > 6 ml. in all instances), a 50-ml. sample would be expected to give a good recovery for toluene and xylene (V_R > 62 ml.) but a low recovery for benzene; this was found to be so.

The retention volumes of a number of compounds were determined (Table I). Substituting $V_s^{\max} = 0.8 V_R$, these results correspond broadly to the equation:

$$\log V_s^{\max} = \frac{\text{b.p. (° C.)} + 13}{70} \quad (2)$$

The actual volume of air required to determine a given compound depends on the detector sensitivity and the maximum permissible concentration; if this volume is less than $V_s^{\max}$ the silicone absorption tube can be used. Our simple apparatus (with sensitivity approximately 3×10^6 mv. ml. per mg.) gave full scale deflection signal for about 2 µg. of a hydrocarbon compound with

a retention time of approximately 5 minutes; if the maximum permissible concentration was 4 mg. per cubic meter—i.e., 1 p.p.m. for a compound of mol. wt. 100—then 500 ml. of air was sufficient and the contaminants in this volume were in general trapped quantitatively if their boiling points were over 176° C. When the maximum permissible concentration was greater than 1 p.p.m. the sample volume was correspondingly reduced and compounds boiling below 176° C. were still retained. Thus, the successful use of a silicone absorption tube packing depended on the particular determination envisaged.

When a compound of relatively low boiling point was being determined, especially at a low level, the volume of sample required to give an adequate signal was sometimes greater than the maximum permissible sample volume for the silicone packing; in these instances, a number of alternatives were possible, and these are treated fully in the Discussion.

Applications. The method described above has been applied so far to 11 instances (19 substances), using the conditions given in Table II. In general, silicone was satisfactory both in the absorption tube and in the column; in some instances the packing in the absorption tube and/or in the column was changed, for the reasons given below.

BENZENE, TOLUENE, AND XYLENE. Since the threshold limit values are relatively high, only 5 ml. of air was necessary, and from this volume these compounds were retained quantitatively by the silicone absorption tube. The components were eluted in the order benzene, toluene, *m*- plus *p*-xylene, and *o*-xylene. The result for *o*-xylene could be obtained by calculation using the areas under the *o*-xylene peak in the test and under the *p*-xylene peak in the calibration. This result was reported separately when required, but normally it would be added to the *m*- plus *p*-xylene result and reported as total xylene concentration.

If the desorption stage cannot be carried out within 2 hours of sampling and/or the 5-ml. sample is too small, a larger sample is taken on a silica gel absorption tube (see below).

TOLUENE CHLORINATION PRODUCTS. The side-chain chlorination of toluene produces benzyl chloride, benzal chloride, and benzotrichloride, and from these are obtained benzoyl chloride and benzaldehyde. In an area where all of these compounds are produced, one or more are liable to be present in the atmosphere, together with toluene, and it is clearly important to distinguish them from toluene and from one another. The threshold limit values for benzyl chloride and toluene are 1 p.p.m. and 200 p.p.m., respectively; no limits have

been declared for the other compounds, but it is likely that not more than a few p.p.m. would be tolerated for the other chloro-compounds, and 1 p.p.m. has been taken as a convenient figure for each chloro-compound.

For the 1-p.p.m. level a 500-ml. sample of air was required, and it will be seen from Table I that the retention volumes for a silicone absorption tube were such that this volume should give quantitative recovery of the chloro-compounds, with benzyl chloride a marginal case. This was found to be so; the compounds were easily separated on the Silicone E.301 column and the peaks appeared in the order: toluene, benzaldehyde, benzyl chloride, benzoyl chloride, benzal chloride, and benzotrichloride. The toluene, if present above about 1 p.p.m., gave an off-scale peak, hence, if its concentration was required a separate test for toluene (as above) was performed. At the 1-p.p.m. level, the chloro-compounds gave peaks about $\frac{1}{4}$ to $\frac{1}{2}$ of full scale deflection. Benzaldehyde was separated from the other components and was detected even at the 1-p.p.m. level; but as expected the recoveries were low, as the retention volume was only 330 ml. (see section on Recoveries).

NITROBENZENE.

ANILINE.

CYCLOHEXANE.

These three substances are grouped together because each could be tested for using the silicone absorption tube and the silicone column. Although the tests have been developed for detecting only the one component in the atmosphere, the retention volume for aniline is about half that for nitrobenzene, so that these two could be determined easily in admixture. Nitrobenzene is, of course, a particularly toxic compound; 0.1 p.p.m. was easily discernible by this test.

PYRIDINE BASES. This is a crude mixture of lutidines, collidines, etc. No special attempt has been made to resolve the individual components (in fact a single peak representing "pyridine bases" would have been preferred) but the silicone column gave an irregular shaped peak showing that partial separation occurred.

CYCLOHEXANONE AND CYCLOHEXANOL. Since these two compounds may well be present in admixture, a good separation on the column was desirable and for this reason poly(ethylene glycol adipate) has been used as the stationary phase.

***o*-DICHLOROBENZENE AND *p*-DICHLOROBENZENE.** The separation of *o*- and *p*-dichlorobenzene is not unduly difficult, but to make the peaks as distinct as possible octadecylamine-ethylene oxide condensate was preferred as stationary phase, since this gave a better separation factor than the other

commonly used stationary phases.

PYRIDINE.

n-BUTANOL.

In both instances the silicone absorption tube was not quite sufficiently retentive so the more retentive polyethylene glycol 400 packing was used instead; this was quite satisfactory provided the desorption heating wattage was reduced to approximately 6 watts by suitable adjustment of the variable series resistance.

HYDROGEN CYANIDE. It was desired to measure HCN in air which could be contaminated with appreciable concentrations of methanol, toluene, and HCl. Since the sensitivity of the flame ionization detector to HCN was only about $\frac{1}{10}$ that of most organic compounds, it was necessary to take a larger sample than hitherto, and it was also particularly important to separate it completely from the organic compounds likely to be present. The silicone absorption tube had a negligible retention volume for HCN at room temperature and therefore silica gel was used. This quantitatively retained HCN from a 1000-ml. sample, and released it completely on heating. To separate HCN from methanol and toluene and still obtain a peak for HCN at a reasonable retention time, adiponitrile was used as the stationary phase in the column, from which the order of elution was: HCN, methanol, toluene. The detector was, of course, insensitive to the HCl.

Reproducibility. The reproducibility of the calibration procedure was assessed by carrying out a series of tests, and measuring the areas (by triangulation) under the appropriate peaks. Most of the results were within $\pm 15\%$ of each mean, which is sufficient for this type of work; there was generally little change from day to day, but it was considered advisable to run a calibration test on the same day as the tests on the atmosphere.

Results Using Standard Toxic Atmospheres. The reliability of the method was checked by carrying out trials using air containing known concentrations of toxic compound(s). These standard atmospheres were made by the controlled fluid-feed atomization procedure of Gage (10), in which a dilute solution of the compound(s) in a volatile solvent in a syringe was expelled at a fixed rate into a metered stream of air by coupling the piston to a Slow Injection Apparatus (C. F. Palmer Ltd., 63A Effra Road, London, S.W.2). Care was taken to ensure that there was no significant leakage of solution past the piston and that adsorption equilibrium had been reached in the apparatus by running it for a short while before sampling. The air supply was checked for freedom from interfering contaminants by carrying out a blank test prior to injection of solution.

As an example of this procedure, a standard atmosphere containing 100 p.p.m. of toluene and 1 p.p.m. of benzaldehyde, benzyl chloride, benzoyl chloride, benzal chloride, and benzo-trichloride was prepared by injecting a stock solution of these compounds in toluene at the appropriate concentration (respectively 0.94, 1.11, 1.25, 1.44, and 1.74% w./v.) at 2.5×10^{-3} ml. per minute into an air stream at 5.5 liters per minute. Tests on these standard atmospheres were carried out by drawing the stipulated volume of the air through the appropriate absorption tube, which was then treated in the usual way immediately after the sampling stage. The results were between 80 and 100% of the expected values, with the following exceptions:

BENZALDEHYDE. The recovery was only 60 to 65%. From the retention volume (Table I) it was expected that some benzaldehyde would emerge from the silicone absorption tube before sampling was complete, and this was shown to be so by carrying out further tests with two absorption tubes in series, when the first tube gave 60% recovery and the second tube about 20%. It was also probable that some of the benzaldehyde was oxidized in the air stream between the fluid-feed atomizer jet and the absorption tube. However, in this particular instance (Table II) it was the determination of the chloro-compounds which was regarded as particularly important, and since the results for these

were not affected by the presence of benzaldehyde, the method as a whole was regarded as satisfactory.

BENZOYL CHLORIDE. The results for benzoyl chloride were also only 60% of the expected values. This could not be due to incomplete retention, since its retention volume was greater than that for benzyl chloride, which gave a satisfactory recovery. The slow formation of a white deposit (presumably benzoic acid) near the jet in the atomizer machine suggested the strong possibility that benzoyl chloride was being lost in significant amount before reaching the absorption tube, due to hydrolysis by the moisture in the air stream.

With the other three chloro-compounds, and indeed in all the other instances given in Table II, the recoveries were 80 to 100%, using various methods of sampling, and this is regarded as quite satisfactory for this type of work.

Storage of Absorption Tubes between Sampling and Testing Stages. Although it is preferable to arrange that the testing of an absorption tube should be carried out as soon as reasonably possible—e.g., within 2 hours—after sampling the atmosphere, it may so happen that testing must be delayed for 24 hours—e.g., if the sampling is necessary at a site some distance from GLC facilities. It was therefore considered necessary to ascertain whether the results on absorption tubes stored after sampling in glass-stoppered test tubes were satisfactory;

tests showed that, with a few exceptions, the tubes could be stored for 24 hours without serious loss of the absorbed compounds. The exceptions were:

BENZALDEHYDE AND BENZOYL CHLORIDE. Storage reduced the recovery to 45% for benzaldehyde and 5% for benzoyl chloride, presumably due to oxidation and hydrolysis, respectively. For a reliable result for benzoyl chloride it is therefore essential to test the absorption tube within 2 hours of sampling.

BENZENE. Gradual loss of benzene was observed from the silicone tube on storage. Although this was not serious, it was considered better to use a silica gel tube, which retained all the benzene (and toluene and xylene) even if 1000 ml. of air was drawn through the tube at room temperature, and which released all of these components rapidly when the tube was heated. It was most convenient to take a 50-ml. sample over 1 minute, to use the apparatus at $1/10$ sensitivity, and to calibrate with a solution 10 times as concentrated as that given in Table II. The reproducibility was still within $\pm 15\%$ in the calibration tests, and recoveries on standard atmospheres were close to 100% even after storage of the absorption tube up to 48 hours.

Gas Sampling Bulbs. In the introduction it is stated that the taking of samples of air in a gas sampling bulb followed by direct injection on a GLC column using a hypodermic

Table II. Experimental Conditions

Compounds under test	Threshold limit values (p.p.m.)	Vol. of air sample, ml.	Time of sampling, min.	Absorption tube packing	Column packing	Temp. of column, ° C.	Sensitivity range used	Standard solution, 0.02 ml. corresponds to threshold limit value in specified air sample volume (except for HCN)
Benzene	25	5	0.5	A (see remarks on storage)	A	65	Max.	0.0023% v./v. benzene, 0.022% v./v. toluene and 0.025% v./v. <i>p</i> -xylene in CS ₂
Toluene	200							
Xylene	200							
Benzaldehyde	—	500	2	A	A	120	Max.	0.46% v./v. benzaldehyde, 0.52% v./v. benzyl chloride, 0.52% v./v. benzoyl chloride, 0.58% v./v. benzal chloride and 0.64% v./v. benzo-trichloride in dry toluene; diluted 44-fold with CS ₂
Benzyl chloride	1							
Benzoyl chloride	} none stated, taken as 1							
Benzal chloride								
Benzo-trichloride								
Nitrobenzene	1	500	2	A	A	120	Max.	0.010% v./v. nitrobenzene in CS ₂
Aniline	5	200	2	A	A	105	Max.	0.019% v./v. aniline in CS ₂ , freshly prepared
Cyclohexane	400	10	0.5	A	A	45	1/10	0.09% v./v. cyclohexane in CS ₂
Pyridine bases	none stated, taken as 10	250	1	A	A	90	Max.	0.067% v./v. pyridine bases in CS ₂
Cyclohexanone	50	125	1	A	B	80	1/10	0.13% v./v. each of cyclohexanone and cyclohexanol in CS ₂
Cyclohexanol	50	125	1	A	C	95	1/10	
<i>o</i> -Dichlorobenzene	50							0.19% w./v. <i>o</i> -dichlorobenzene and 0.28% w./v. <i>p</i> -dichlorobenzene in CS ₂
<i>p</i> -Dichlorobenzene	75							
Pyridine	5	125	1	D	D	75	Max.	0.01% v./v. pyridine in CS ₂
<i>n</i> -Butanol	100	125	1	D	D	60	1/10	0.23% v./v. <i>n</i> -butanol in CS ₂
Hydrogen cyanide	10	1000	4	Silica gel	E	20	Max.	0.004 ml. of 0.28% w./v. HCN in methanol

Code for packings: (details as under Apparatus and Materials)

A = Silicone Elastomer E.301.
B = Poly(ethylene glycol adipate).
C = Octadecylamine-ethylene oxide condensate.
D = Polyethylene glycol 400.
E = Adiponitrile.

syringe results in losses, particularly with higher-boiling compounds. To illustrate this, a standard atmosphere containing benzene, toluene, and *p*-xylene (25, 100, and 100 p.p.m.) was stored in two 300-ml. gas sampling bulbs, with taps at each end; bulb A contained a short central side-arm over which was fitted a rubber serum cap and bulb B was fitted with a rubber serum cap over the glass tubing at one end of the bulb so that the serum cap and the sample in the bulb were separated by a tap. At intervals, 5-ml. samples were removed via the serum cap using a hypodermic syringe (inserted also through the bore of the tap in bulb B) and injected into the GLC apparatus, the difference between the two sets of tests was that with bulb A the sample was in contact with the serum cap during the entire storage period, whereas with bulb B the contact was only momentary during withdrawal of the samples for injection. The recoveries were calculated by comparison with the results using a standard solution; the recoveries obtained with bulb B were fairly satisfactory up to 24-hour storage, but those obtained with bulb A became substantially lower—e.g., 20% for toluene and for xylene—after storage for 24 hours, presumably because of the prolonged contact with the serum cap. It is clearly inadvisable to use bulbs of type A for collecting atmosphere samples prior to testing.

Although bulbs of type B may be satisfactory, adsorption losses may occur with higher-boiling compounds when transferring samples by means of a hypodermic syringe. Thus, a 50-ml. sample of air containing 20 p.p.m. nitrobenzene was injected into a GLC column, the syringe was then filled with 50 ml. of uncontaminated air, and the contents were injected after 5 minutes; the syringe was again filled with 50 ml. of air and the contents were injected after 5 minutes. The peak heights from the second and third fillings were 27% and 10% of the original peak height, reflecting considerable retention of nitrobenzene in the syringe after the first injection. Similar results were obtained using other compounds. To avoid risk of such losses, we reject the sampling bulb hypodermic syringe technique.

DISCUSSION

The data given in Table I for a 1-inch silicone absorption tube show that, with a few exceptions, the maximum permissible sample volume of a given organic compound is related to the boiling point of the compound according to Equation 2 above; this is in accordance with the known property of the silicone stationary phase of eluting compounds generally in the order of their boiling points. It is therefore possible

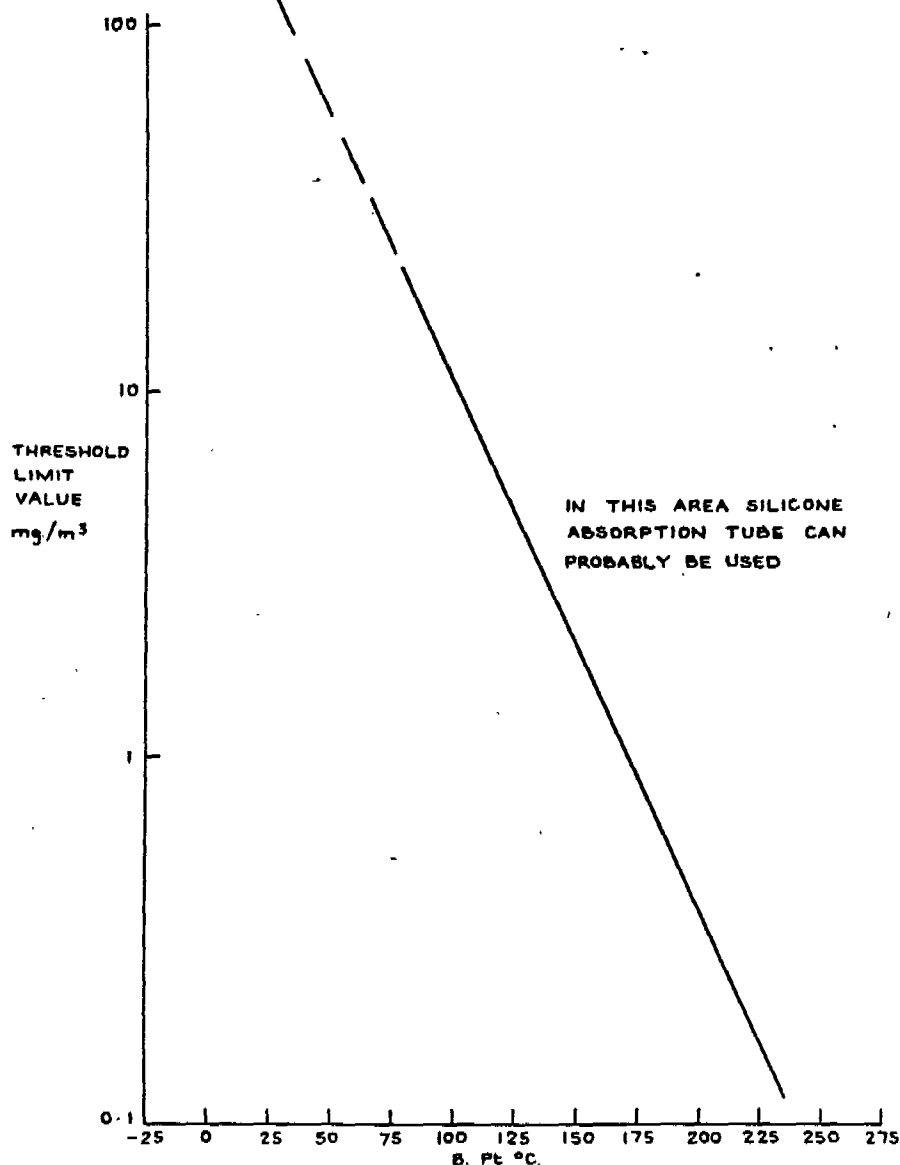


Figure 4. Relationship between b.p. and threshold limit values, for 1-inch silicone absorption tube

to predict whether a silicone absorption tube is likely to prove suitable in further applications.

If the sensitivity of the detector and the operating conditions are such that full scale deflection will be given by W μ g. of compound and if the threshold limit value is C mg. per cubic meter, it follows that full scale deflection will be given for a sample volume of W/C liters of air. Since $1/5$ of full scale deflection may be taken as a convenient minimum peak size for detecting C mg. per cubic meter, the corresponding sample volume should be $\frac{1000W}{5C}$ ml., and the silicone tube is likely to prove suitable if this volume does not exceed $V_3^{\max}$ —i.e.,

$$\text{provided } \log \frac{200W}{C} > \frac{\text{b.p.} + 13}{70}$$

$$\text{or b.p.} < 148 + 70 \log W - 70 \log C$$

With our apparatus W may be taken as 2 (for the convenient column retention time of 5 to 10 minutes) and hence a silicone absorption tube can probably be used provided the boiling point is not less than $169 - 70 \log C$. Figure 4 shows this relationship in the form of a demarcation line, the extrapolated portion of which is shown as a broken line; if the point on this figure corresponding to the boiling point and the threshold limit value for a given compound lies to the right of the line, the silicone absorption tube can probably be used; it is necessary, of course, to establish experimentally in each case that the retention is complete using the appropriate sample volume. If the point lies to the left of the line the silicone absorption tube is likely to prove unsatisfactory, the degree to which this is so increasing with increasing distance of the point from the line.

In the list of threshold limit values for 1961 (17)—including the tentative values—carbon monoxide, carbon dioxide, carbon disulfide, phosgene, and nickel carbonyl can be regarded as inorganic; there are thus 164 organic gases and vapors in the list and of these only the following 21 compounds (Table III) lie to the left of the line (arranged in increasing distance from the line).

In addition to the 21 compounds, there are 7 others which (although they lie to the right of the line and thus are determinable in principle with the silicone absorption tube) have such low boiling points that the corresponding maximum permissible sample volume is inconveniently small to sample; the minimum convenient sample volume can be taken as 5 ml., and substitution in Equation 2 shows

Table III. Organic Compounds Lying to the Left of the Demarcation Line of Figure 4

	Boiling point, °C.	Threshold limit, mg./m. ³
Butylamine	77	15
Dichlorodifluoromethane*	-30	4,950
Perchloromethyl mercaptan	159	0.8
Methyl mercaptan	8	100
Ethylene oxide	11	90
Allyl alcohol	96	5
Trifluoromonomethyl bromomethane*	-58	6,100
Ethylamine	17	45
Methyl chloride	-24	210
Allyl chloride	45	15
Methyl bromide	4	80
Ethylene imine	56	9
Tetranitromethane*	126	8
Chloroacetaldehyde	85	3
Isopropylamine	34	12
Chloropicrin	110	0.7
Dimethylhydrazine	62	1
Acrolein	52	1.2
Formaldehyde	-21	6
Hydrogen cyanide*	26	11
Ketene	-50	0.9

* Appropriate allowance has been made for tetranitromethane, hydrogen cyanide, and the fluorinated hydrocarbons, which give a low response to the flame ionization detector (approx. 1/10 of that of most organic compounds).

Table IV. Compounds with Maximum Permissible Sample Volume less than 5 ml.

	Boiling point, °C.	Threshold limit, mg./m. ³
Fluorotrichloromethane	24	5,600
Ethyl chloride	13	2,600
Dichloromonofluoromethane	9	4,200
Dichlorotetrafluoroethane	-2	7,000
Butadiene	-3	2,200
Vinyl chloride	-14	1,300
Methyl acetylene	-23	1,650

that the corresponding minimum boiling point is 30° C. The compounds in this category are shown in Table IV.

Subtracting the above 28 substances from the 164 listed leaves 136 substances—i.e., 83%—which it is concluded can be determined in principle with the silicone absorption tube. In practice it is envisaged that certain experimental difficulties may arise in a few instances—e.g.,

The substance may be oxidized or hydrolyzed in the silicone absorption tube during the interval between sampling and testing; benzoyl chloride has been shown above to behave in such a manner, and possible compounds falling in this category are acetaldehyde, acetic anhydride, dimethyl sulfate, and tolylene di-isocyanate.

The substance, being a mixture, may give several partially separated peaks, thus making calibration difficult; coal tar naphtha, petroleum naphtha, gasoline, turpentine, and Stoddard solvent fall into this category, but since the mixture constituting pyridine bases has been determined successfully above, so by analogy should these other mixtures.

If it is desirable in certain investigations to determine actual concentrations below the threshold limit—i.e., not merely to report that the atmosphere contains less than the threshold limit—it would be necessary to arrange conditions so that the compound at the threshold limit gives say a full-scale instead of a 1/4 deflection signal. With those compounds which lie well to the right of the demarcation line this could be done simply by increasing the sample volume accordingly, since this will generally be much lower than the maximum permissible sample volume; for high-boiling compounds, the sampling time could be kept short by increasing the sampling rate to for example 1 to 2 liters per minute, by replacing the compressed 100- to 120-mesh Celite in the absorption tube by loosely-packed 30- to 60-mesh Celite. For those compounds which lie just to the right of the demarcation line, however, it would be necessary to use one of the modifications suggested below for detecting the remaining 28 compounds.

It has been shown above that the majority of the organic compounds in the list of threshold limit values (17) can be retained by the silicone absorption tube. The method could be extended to cover some of the 21 compounds of Table III by using a more sensitive apparatus (with a smaller sample volume), but such apparatus would be more expensive, less portable and more subject to noise arising from thermal instability of the packing. It is considered that it would be preferable to modify the conditions so that the maximum permissible sample volume is increased, and this can be done in three ways:

1. *Reducing the temperature of the absorption tube below ambient by special cooling.* This is regarded as the least attractive since it would involve redesigning the shape of the absorption tube and desorption heater, and would result in considerable inconvenience when sampling at a distance from laboratory facilities.

2. *By increasing the amount of stationary phase.* The amount of stationary phase on the Celite 545 (30% w./w.) is already near the maximum loading, but it would be possible to replace the Celite by a solid support of greater packing density; thus Silocel C22 Firebrick (L. Light & Co. Ltd., Colnbrook, Bucks., England) and Chromosorb P (Johns-Manville Corp.) are both approximately 1.5 times as dense as Celite 545. However, it has been claimed that firebrick and some varieties of kieselguhr are unsatisfactory as solid supports, particularly in work on nonhydrocarbons, since they exert a catalytic effect (probably dehydration) on the decomposition of certain oxygenated compounds (14). Although various methods of treating the support have been reported, these have not been tried in this work.

3. *An alternative way of increasing the amount of stationary phase would be to use a larger absorption tube.* However, by increasing the length of the tube and correspondingly increasing the sample volume to a value near the maximum permissible, the compound would be distributed over a longer length of the packing, and desorption would necessarily result in the introduction of the compound on to the GLC column over a more prolonged charging period, with a consequent increase in the peak width; this would ultimately affect the separation between two adjacent peaks—e.g., of *o*- and *p*-dichlorobenzene. A similar effect would be obtained by increasing the diameter of the tube, since the packing will take longer to heat towards the center. If the central portion did not become hot enough, recovery would be incomplete, and if the desorption wattage were increased to overcome this, the packing next to the tube wall might become hot enough to cause thermal breakdown (with consequent reduction in sensitivity and increase in noise).

4. *By using a more retentive stationary phase or a solid adsorbent.* Silicone gives significantly lower specific retention volumes than the other common stationary phases, as exemplified by the values for *p*-xylene at 100° C. on 6 stationary phases (14). The difference between silicone and the other stationary phases is, of course, more marked if both the solute and the other stationary phase are polar—e.g., the retention volume of pyridine on polyethylene glycol 400 has been shown to be five times that on silicone. However, these other stationary phases are less thermally stable—i.e., they and their associated impurities are more easily volatilized and/or pyrolyzed during the desorption stage—and Silicone Elastomer E.301 is therefore the first choice in most instances. Nevertheless, other stationary phases, particularly polar

ones, can prove very useful in certain circumstances—for example, for *n*-butanol and pyridine—for which polyethylene glycol 400 has been used (Table II). The polar stationary phase of greatest thermal stability so far examined is Neoplex 400 (ex Geigy Ltd.) and this would now be regarded as first choice when seeking an alternative to silicone.

Of the 28 compounds for which silicone is probably unsuitable, most of those in Table IV and some of those in the upper part of Table III could probably be detected using a suitable polar stationary phase. The remainder would probably prove insufficiently retentive on any gas-liquid partition system and for these a gas-solid adsorption system may be effective. This work contains one example in this category—i.e., HCN—which was adsorbed on silica gel, and it is therefore relevant to discuss certain aspects of the behavior of such adsorbents.

The two most useful adsorbents are silica gel and activated carbon, which differ in several respects. Silica gel is polar and will consequently show pronounced selectivity in preferentially adsorbing polar molecules, in particular water. Hence, when sampling large volumes, the atmospheric moisture may compete for the adsorption sites and displace the toxic compound being sought, especially if this is nonpolar. Thus, it can be shown that the silica gel absorption tube described above may become saturated with water when the sample volume is only 3 liters, and the retentive properties of the silica gel may be impaired as sample volumes of this size are approached. Desorption from silica gel is relatively easier than for carbon, but will be more difficult for the more strongly held polar compounds; thus it has been shown that *o*-dichlorobenzene can be readily desorbed from silica gel with 2 minutes heating at 12 watts whereas compounds of similar boiling point but with chlorine in the sidechain instead of the nucleus—e.g., benzyl and benzal chloride—cannot be desorbed even with 5 minutes heating at 18 watts.

Activated carbon is nonpolar and will consequently generally adsorb organic vapors in preference to water, so that atmospheric moisture will not interfere with the sampling of large volumes; however, desorption is generally more difficult than from silica gel.

Although the adsorptive capacities of both silica gel and activated carbon will be much greater in general than the amount of toxic compound to be adsorbed, in practice it will be their retentivities—i.e., the maximum amount of the compound retained when exposed to uncontaminated air (18)—that will decide their suitability, since the concentration of toxic compound in the sample volume will always be

Retentivity values for a number of compounds on 6- to 14-mesh carbon have been tabulated (1). Since the system is a dynamic one, the rate of adsorption will limit the sampling flow rate. From the information in (1), it can be shown that, with our absorption tube, the sampling rate should not exceed 70 ml. per minute and in many instances, particularly with compounds boiling below 0° C., it would have to be much lower than this, necessitating excessively long sampling times. In some instances the tube would have to be lengthened and/or the carbon cooled or impregnated—e.g., with bromine, for retaining olefines. Similar considerations will no doubt apply to silica gel.

Losses due to irreversible adsorption at the desorption temperature, or to catalytic reaction on the adsorbent surface—e.g., olefin polymerization on silica gel—may render an adsorbent unsuitable; the catalytic effects may be reduced by using specially purified gel (Davison grade 923) although even with this material, evidence was obtained that *n*-butanol was catalytically dehydrated to butene. Activated carbon which has been specially processed to minimize catalytic activity is available (from Carbide and Carbon Chemicals Co., New York).

It is clear from the above considerations that the use of solid adsorbents as tube packings cannot be treated in as general a manner as the gas-liquid partition packings, and that each toxic compound must be tested for retention volume, sampling time, storage stability, and completeness of desorption.

Toxic Dusts, Fumes, and Mists. The method is in principle applicable to some of the organic dusts, fumes, and mists in the list of threshold limit values (17), since such particulate matter is expected to be trapped by the absorption tube, probably in the inlet plug. Desorption should not prove difficult, since even chrysene (b.p. 450° C.) can be 80 to 90% desorbed from a silicone absorption tube under the standard conditions. However, the desorption heater should be made longer so that the inlet plug is properly heated.

Automation of the Method. The method described above could be adapted into a unit which would monitor a plant atmosphere every 15 minutes, for example. It is envisaged that a sampling valve would be made with appropriate slots or grooves cut into a polytetrafluoroethylene sliding plate sandwiched between two stationary metal plates, one of which carries a thin metal loop, say 5-mm. bore and 1½ inches long. The other plate would carry ports to allow the carrier gas stream to pass into the column, and to allow the air stream to be drawn through the loop by a vacuum pump. The loop would be charged

with the stationary phase or silica gel, and would be wound so that it could be electrically heated when desired. A glass or metal column, with the appropriate packing, would be attached to a flame ionization detector fitted with a flame-proof housing with nitrogen flowing in the annular space. Nitrogen would be used as carrier gas and the required flow of hydrogen would be fed in between the column exit and the detector jet, thereby ensuring that the flame would not be extinguished when the sample valve operates. A motor-driven timing device would actuate the sampling valve and also switch on and off the heater around the loop. The signal from the detector would preferably be fed via a relay into an audible alarm system, adjusted so as to operate only when the signal exceeds a specified value during a specified period.

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