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SAMPLING OF AIR POLLUTANTS WITH SUPPORT-BONDED CHROMATOGRAPHIC PHASES*

WALTER A. AUE AND PANKAJ M. TELI**
University of Missouri, Columbia, Mo. 65201 (U.S.A.)

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SUMMARY

Support-bonded silicones, such as $(C_{18}H_{37}SiO_{3/2})_n$ on various types of Chromosorb, can be used to trap organic vapors from the atmosphere. The trapped compounds can then be extracted and the concentrated extracts analyzed by various analytical techniques.

INTRODUCTION

Organic materials are present in the atmosphere either as aerosols or as vapors. Vapors are generally the more difficult to collect and the literature on them is scant in comparison to the information available on particulates. Several reviews on air pollutants are available[1-6], some of which refer to the sampling question.

The collection and analysis of organic vapors, especially those of higher molecular weight, can be fairly difficult. The troubles stem mainly from the ubiquitous presence of water in the atmosphere and are aggravated by high concentrations of oxidants, sulfur oxides, nitrogen oxides, etc. Organics of higher molecular weight are present in minute amounts only, and some of them can easily decompose. Furthermore, sampling outside the realm of the laboratory can present additional problems. Yet, the organic composition of air in remote locations holds considerable interest for various branches of science.

This paper reports an attempt to develop a simple method for collection of organics from air (or from other gases), a method which could be used at ambient temperature in remote locations and would provide the analyst with enough material for several analytical tests. In our case, these tests were based on gas–liquid chromatography (GLC).

The methods reported in the literature rely on liquid traps, cold traps, or adsorbents. A special place is occupied by methods using gas chromatographic (GC) phases, on which organics are collected[7-17]. The collected materials can then be swept

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into a GLC column by sudden heating. This approach gives excellent sensitivity, but limits the amount of obtainable information.

Obvious advantages could be gained by using greater amounts of GC phases and extracting, rather than volatilizing the collected air pollutants. The concentrated extracts could then be analyzed by different methods. The solubilities of GLC phases in suitable solvents, however, do not generally permit such an approach. Support-bonded phases, on the other hand, are non-extractable per definition and should be well suited for sampling. (Short reviews of these literature of these phases can be found in refs. 18 and 19.)

To perform well in the collection of air pollutants, a support-bonded liquid phase should ideally (a) be present in great amounts (very high load) to effect maximum retention, (b) be bonded to a coarse support to permit rapid gas flow (sampling rate), (c) yet allow complete equilibration of organic vapors between gas and liquid phases, and (d) be generally resistant to attack by reactive air pollutants such as oxidants, sulfur dioxide, etc. It has to be truly support-bonded, of course, *i.e.* exhaustive extraction with various solvents must fail to remove any traces of polymer.

Various materials developed in our laboratory[18,20] have met this test of support-bonding. After an initial extraction to remove non-support-bonded polymer (which is always present to some extent), the materials could not be further extracted by solvents of various polarities in 48-h Soxhlet or 16-h Goldfisch extractions. The liquid polymer load was then estimated from the weight loss incurred by a 1000° heat-treatment for 3 h.

Initial sampling experiments with support-bonded phases were carried out some time ago[21]. They followed the schema shown in Fig. 1 for test, collection, and extrac-

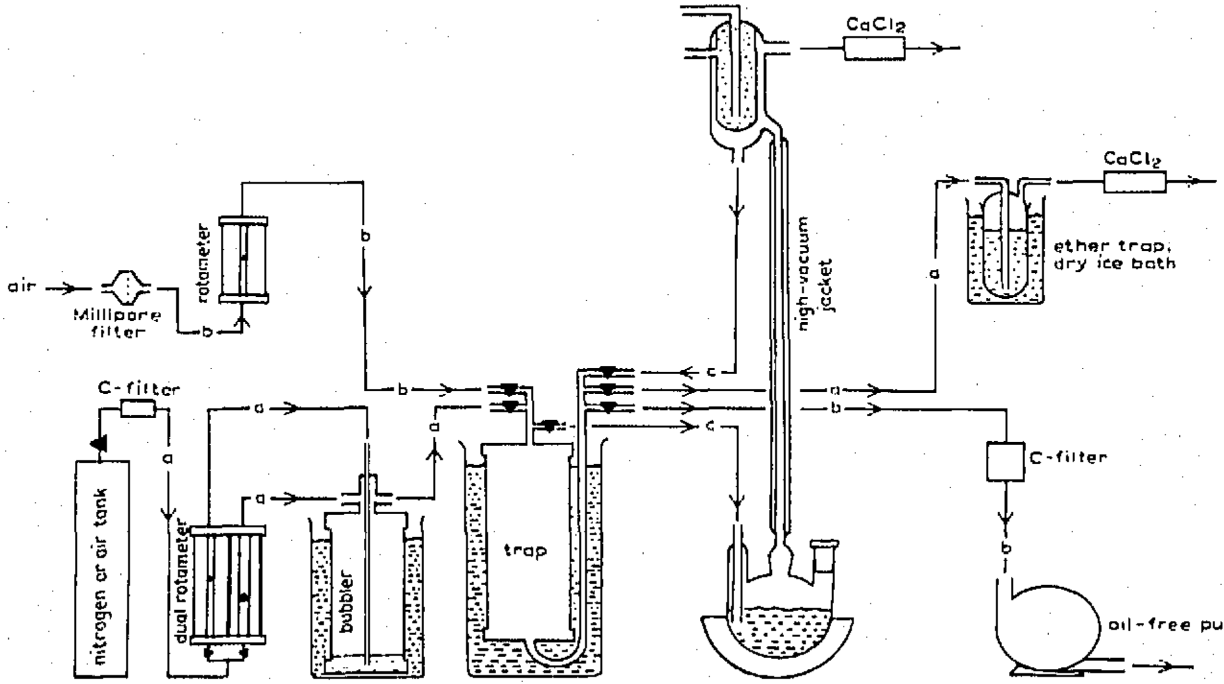

Fig. 1. Initial laboratory set-up for collecting organics on, and extracting them from, support-bonded silicone phases contained in the "trap". a, Test compound sampling; b, atmosphere sampling; c, extraction.

tion procedures. The flow-chart is largely self-explanatory, but it should be noted that the solvent used for extraction flows upwards through the trap, in a direction opposite to the original gas stream used in sampling. The amount of solvent is held to a minimum by re-cycling, and is further reduced by withdrawing only the contents of the three-necked flask for GLC analysis and discarding the essentially pure solvent left in the trap.

These experiments showed that it was indeed possible to retain a variety of compounds in the trap, *i.e.* the cartridge containing the support-bonded phases. Starting from these basic experiments, the present paper describes the simplification of the hardware for field sampling, the demonstration of analytical applicability, and the more elaborate testing of collection efficiency.

To determine efficiency in the laboratory is relatively simple. In the field and with unknown compounds, however, approaches other than a terminal cold-trap on the collection train are called for. One easy way out is to connect two cartridges in series, whereby the extract from the second cartridge can indicate which compounds have been partially and which ones have been totally retained in the first cartridge. A generalized picture of the two-cartridge approach is shown in Fig. 2. To test the performance of support-bonded phases with this approach, complex mixtures of organics with a wide range of boiling points can be used — as exemplified by gasoline or car exhaust.

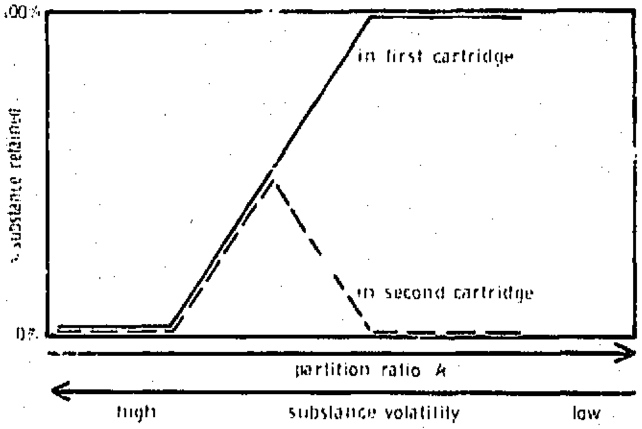

Fig. 2. Scheme of the retention of compounds according to their partition ratios. It is assumed that two identical cartridges containing the support-bonded phases are arranged in series, and the gas stream flowing through them contains constant amounts of organics.

It should be understood that some of the methods mentioned in this paper — *e.g.* the determination of sampling rate with balloons or the GLC analysis with packed columns — are certainly not the ones to choose for the quantitative measurement or qualitative identification of air pollutants, respectively. They served well, however, for demonstrating the capabilities and limitations of the system under scrutiny.

EXPERIMENTAL

Initial experiments

Initial experiments were conducted with the set-up shown in Fig. 1. In one experiment, a mixture of the test compounds phenol, aniline, acetophenone, and naphthalene was introduced into the cartridge from a heated bubbler in the first minutes of sampling. Sampling times were 90 min at either 4, 10, or 20 l per minute of nitrogen. At ambient temperature, all compounds were collected virtually quantitatively at the low flow rate, while only partial retention was achieved for acetophenone at the medium flow rate. Acetophenone was lost, and naphthalene only partially retained, at the high flow rate. When the same experiments were run with uncoated support (Chromosorb blank), no compounds were retained in the cartridge.

Another experiment was designed to define the time necessary for extraction with pentane. After the four test compounds listed above had been collected in the cartridge, the counter-current stream of solvent was turned on and samples were taken at regular intervals from the flask through a septum-type arrangement affixed to its third neck. The GLC of these samples showed that the test compounds had transferred to the flask completely 10 to 15 min after the cartridge overflowed.

A third experiment was designed to show any losses of volatile compounds during the extraction and concentration steps. A series of hydrocarbons from n-C_7H_{16} to n-$C_{12}H_{26}$, 0.2 mg each, were dissolved in 200 ml pentane and used to simulate the extraction and concentration procedures. Taken to 1.0 ml, the extract was chromatographed and failed to show any significant losses.

Apparatus

Fig. 3 shows a set-up typical for sampling of car exhaust or the atmosphere. Bell & Gossett Models SY-C-21-1 or SY-C-20-1 oil-free pumps were connected with

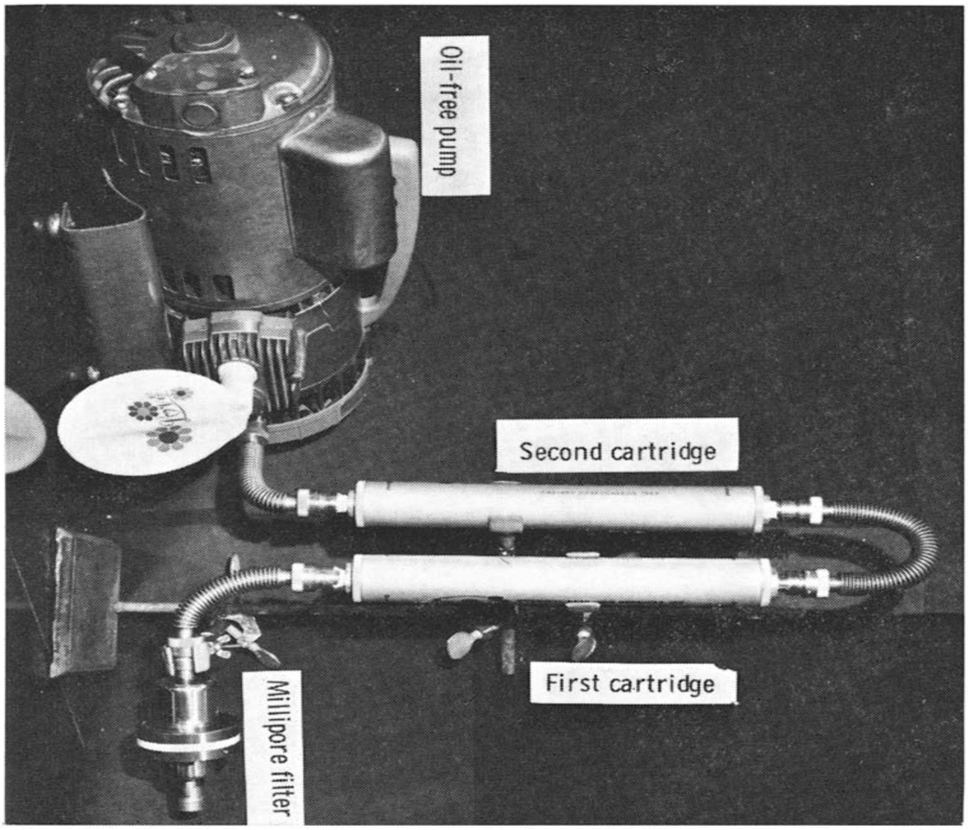

Fig. 3. Typical set-up for atmospheric sampling. The deflated balloon shown is used to roughly estimate the air flow rate for each sampling experiment.

Cajon fittings and flexible stainless-steel tubing to two cartridges containing the support-bonded phases, held in place by stainless-steel screens and glass wool. The flow rate was estimated by measuring the diameter of inflated balloons attached to the pump for a measured time. Air entered the system through a teflon Millipore filter of 5-μ pore size, which was supported by a stainless-steel screen in a modified Millipore filter holder. The cartridges were Chemical Research Service "hydrocarbon traps". Teflon is the preferred material for the packing rings; if silicone rubber is used, it should be covered by teflon tape to avoid extraneous GLC peaks. The O-rings in the fittings are somewhat less prone to cause trouble. All Cajon fittings and flexible tubing were 1/2 in. nominal, making for facile set-up, take-down, or interchange, of the system components.

Fig. 4 shows the set-up used for extraction of collected organics from the traps. The three-necked flask had Clearfit joints, precluding the need for grease. A high-vacuum jacket surrounded the distillation column to avoid excessive reflux. Teflon tubing and adapter ferrules (Scientific Research Service) were used for connections via

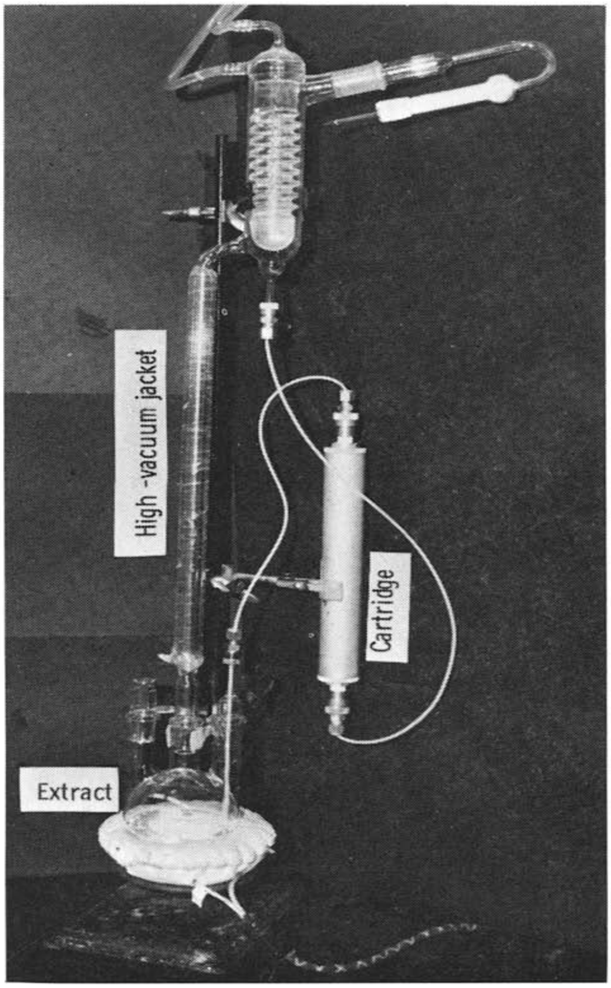

Fig. 4. Set-up for extraction of collected air contaminants. Freshly distilled solvent enters the cartridge at the bottom and overflows back into the flask.

Swagelok fittings with 1/2 in. tube extensions. Since these extensions match the Cajon fittings on the cartridge, the latter could be inserted or removed without the use of tools in less than a minute. A brisk flow of solvent — pentane or other liquids of high purity and volatility — was maintained for approximately 15 min after the cartridge overflowed into the flask.

The pentane extract was concentrated, first in a flask and then in a graduated tube, to *ca.* 0.3 ml or less by blowing dry, pure nitrogen at the surface of the liquid. If further concentration was required, the extract was transferred to a capillary tube and concentrated with nitrogen introduced through a syringe needle.

Other conditions for sampling and/or GLC analysis are described below or in the legends to Figs. 5–12.

Gasoline and car exhaust sampling

These experiments were performed mainly to indicate the volatility range subject to collection, as determined by the two-cartridge approach (Fig. 2) with a complex mixture of organics.

Gasoline was introduced to the cartridges via a heated bubbler similar to the one shown in Fig. 1. The small amount volatilized within a few minutes, but the flow of nitrogen was kept up for 2 h. The GLC analysis of the two cartridge extracts is shown in Fig. 6.

Car exhaust was sampled by connecting the Millipore filter holder to a funnel, which was positioned above the exhaust pipe of an idling V-8 Dodge Dart or six cylinder Chevrolet Malibu. Two typical examples are shown in Figs. 7 and 8 of materials collected from these two cars under different conditions of time and temperature.

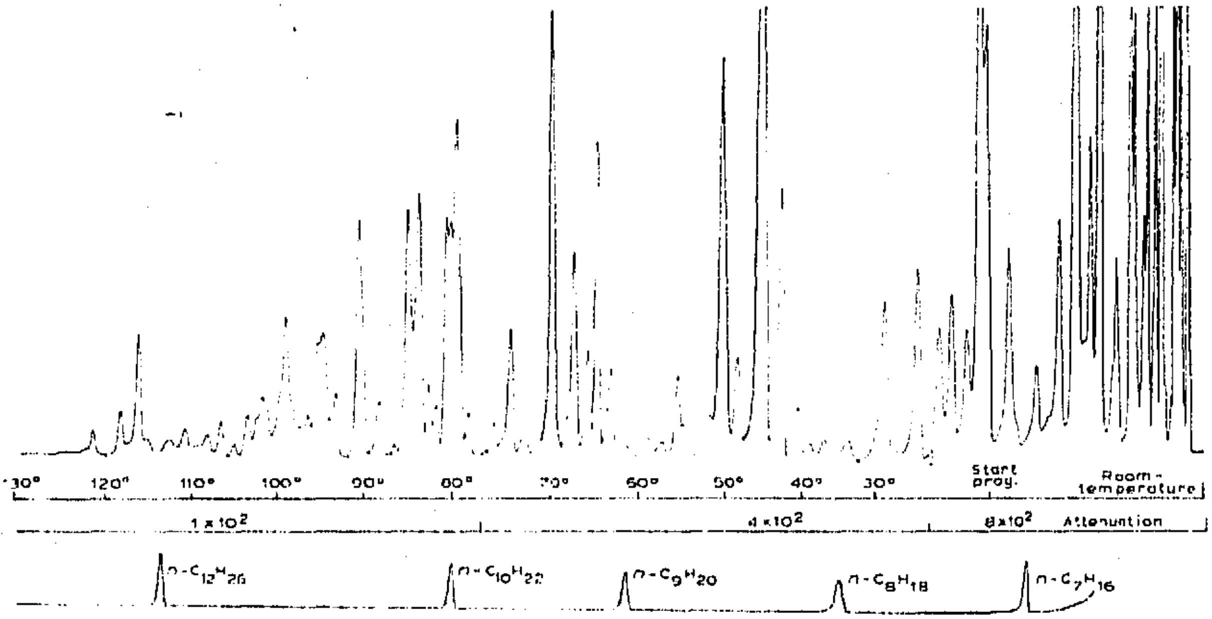

Fig. 5. Gas chromatogram of regular gasoline used in subsequent experiments (Figs. 6 and 7). GC conditions: 3% OV-101 on Chromosorb W-HP, 80/100 mesh, 20 ft. × 2.5 mm I.D. Pyrex; nitrogen flow optimized, 10 ml/min; flame ionization detector.

Further experiments with car exhaust

These experiments were done to demonstrate — basically to ourselves — that extracts of organics collected on support-bonded materials could be analyzed by different analytical methods.

Car exhaust extracts were examined by combined GLC–MS, using a CEC 110 double-focusing mass spectrometer coupled to a Packard gas chromatograph via a Watson–Biemann separator. They were further analyzed for sulfur compounds with a Melpar flame photometric detector, and for phosphorus compounds with a flame photometric and an alkali flame detector. In another experiment, effluents from the GLC column were split between flame ionization and ^{63}Ni electron capture detectors. The split ratio was set by a Precision Sampling high-temperature valve situated within the column oven but operated from the outside. A typical dual-channel chromatogram is shown in Fig. 9.

Collection of chlorinated hydrocarbons

Atmospheres containing known levels of chlorinated hydrocarbon insecticides are difficult to control. Therefore, a number of these compounds were introduced into a fast air stream by a slow stream of nitrogen purging a heated "bubbler"

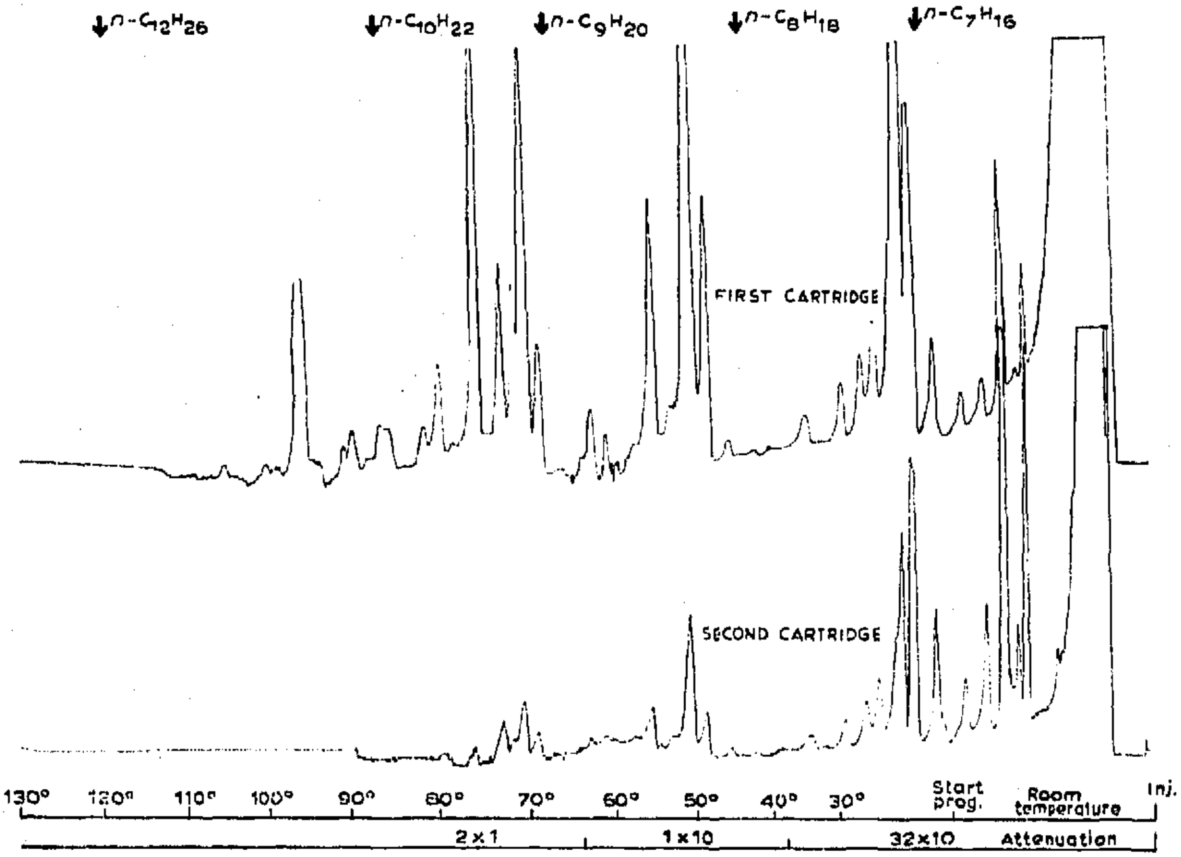

Fig. 9. Gas chromatograms of regular gasoline components collected from a gas stream by two cartridges arranged in series. 2 ml gasoline were initially introduced in a nitrogen stream, comprising *ca.* 420 l within 2 h. The identical cartridges contained 24% $(C_{18}H_{37}SiO_{3/2})_n$ on Chromosorb A, 20/30 mesh. GC conditions as in Fig. 5.

(*cf.* Fig. 1). The collection train included the bubbler, a Millipore filter, two cartridges, a dry ice trap to make students in the laboratory feel at ease, and finally, the pump, placed in a hood. The results are shown in Fig. 10.

Sampling of atmospheric contaminants

A number of air samples were procured with the set-up shown in Fig. 3, both in Columbia, Mo. and in St. Louis, Mo. Two typical examples are shown in Figs. 11 and 12. The second cartridges of the St. Louis sample contained only traces of materials, except for a heavy contribution of the first peak from the industrial area, appearing at *ca.* 145 in the chromatogram. No attempt was made to identify the compounds.

Other experiments

It was noted that sometimes in atmospheric samples peaks would show up which, due to their regularity of appearance in the temperature-programmed chromatograms, were suspected to arise from an interaction of an inorganic air pollutant with the support-bonded octadecylpolysiloxane. Consequently, very heavy amounts of sulfur dioxide and nitrogen dioxide in air were blown within 2 h through the cartridges and their effects examined. Nitrogen dioxide showed no effect; sulfur dioxide (or its reaction products with the atmosphere) caused peaks. Only some of them, however, corresponded in retention time to the suspected artifacts. These compounds

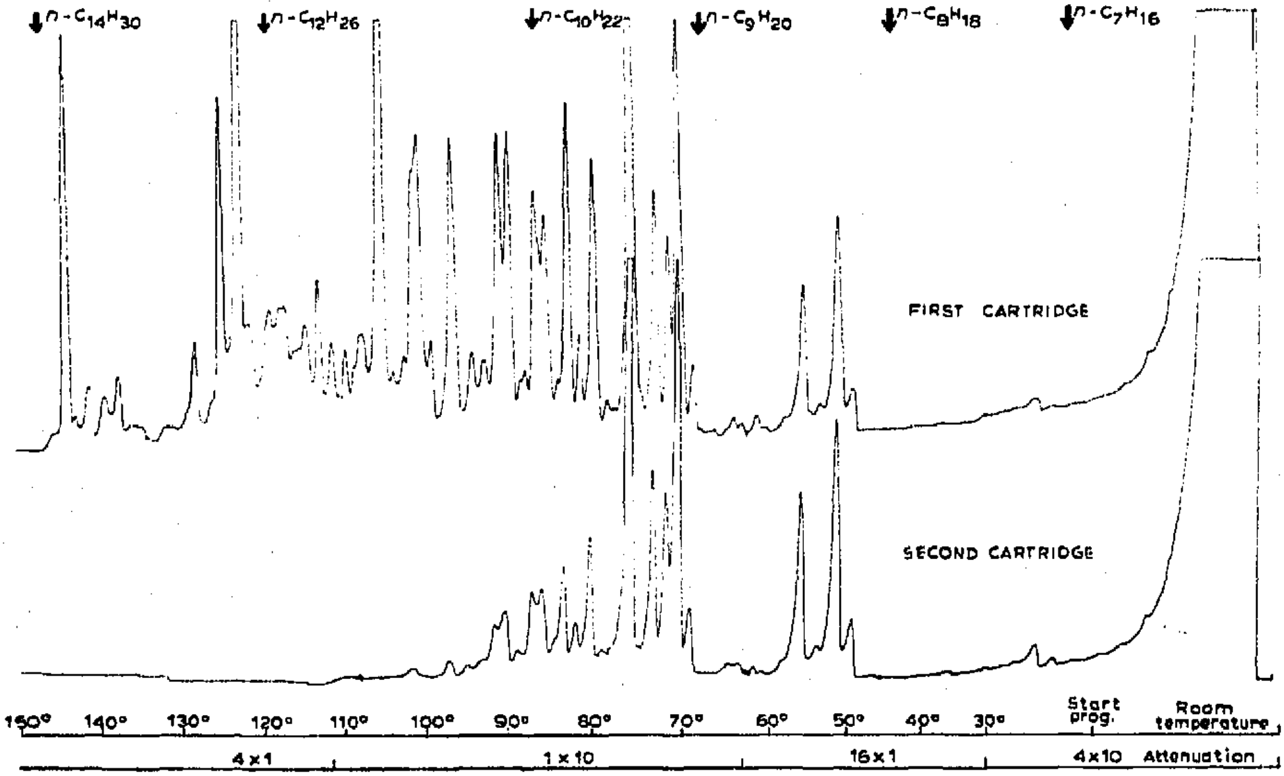

Fig. 7. Gas chromatograms of car exhaust components collected on two identical cartridges containing 24% $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb A. Sampling time, 60 min at 30 l/min. The injections represent *ca.* 0.16 sec of sampling. GC conditions as in Fig. 5.

can be removed from the extract, incidentally, by column chromatography on silica gel.

RESULTS AND DISCUSSION

There are two problems yet associated with the described technique of retaining organic vapors from air on support-bonded silicones. One, the occasional occurrence of artifacts, is cited immediately above. No definite conclusions could yet be reached, but this problem is subject to further study on the nature and the origin of these small, but irritating GLC peaks. The investigation of support-bonded phases other than the one derived from octadecyltrichlorosilane may elucidate or alleviate the situation.

The second problem — which actually could be considered an advantage in certain cases — is the limitation of the method to the less volatile components of the atmosphere. Certainly one could extend the range by cooling the cartridge, increasing its length, or using polymers with better retention characteristics. If these measures were successful, however, a problem would ensue in the extraction with pentane.

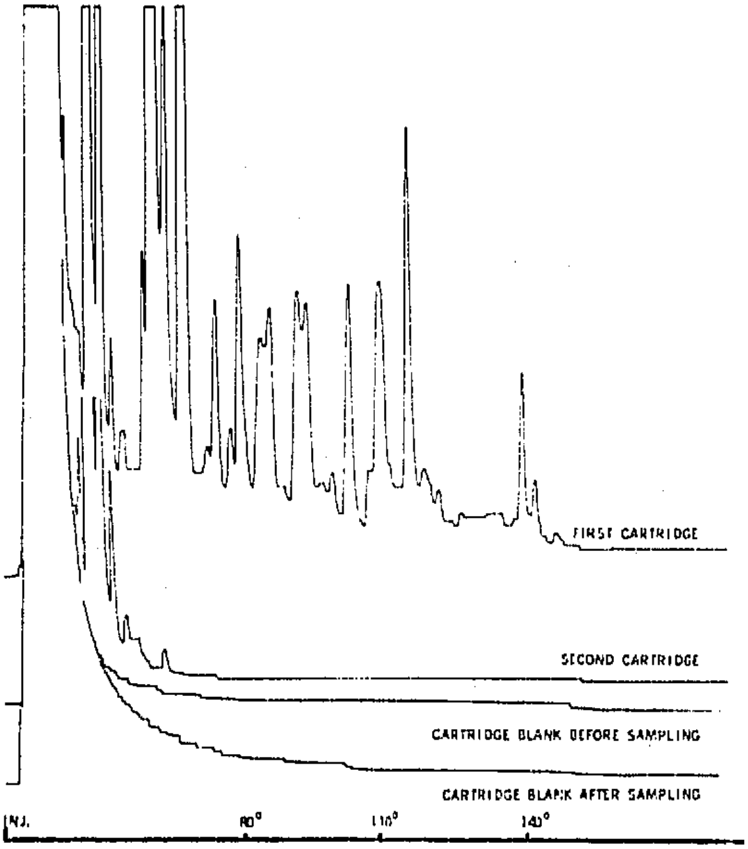

Fig. 8. Gas chromatograms of car exhaust components collected on 26% $(C_{18}H_{37}SiO_{3/2})_n$ on Chromosorb W, 30/60 mesh in the first cartridge and 28% $(C_{18}H_{37}SiO_{3/2})_n$ on Diatom W, 20/40 mesh in the second cartridge. Sampling rate, 10 l/min; sampling time, 10 min. Injections represent 0.12 sec of sampling; GC conditions: 3% OV-101 on Chromosorb W-HP, 80/100 mesh, 10 ft. × 2.5 mm I.D. Pyrex; nitrogen flow 40 ml/min, FID.

followed by concentration and GC analysis. Obviously, any compound of higher volatility than, say, heptane, would be subject to losses.

Aside from these two problems or limitations, the method as described proved to be a simple and efficient technique for the collection and analysis of organic compounds of higher molecular weight from gaseous systems. The unique characteristics of heavy loads of support-bonded silicones — long retention times in GC, short retention times in liquid chromatography, and, of course, their non-extractability — make them excellent candidates for such a task. The phases can be used over and over again and we assume — from their behavior in GLC — that they would not induce decomposition reactions as are known to occur, for instance, on activated carbon.

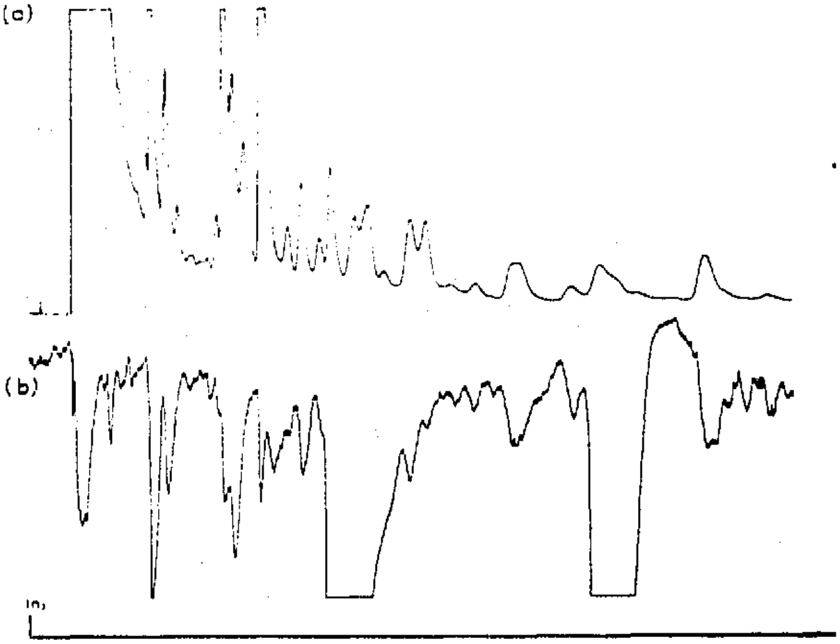

Fig. 9. Isothermal gas chromatogram of car exhaust extract (same as shown in Fig. 7, first cartridge). The injection represented 0.54 sec of exhaust sampling and was split in a ratio of *ca.* 2:1 between a flame ionization (a) and a ^{63}Ni electron capture detector (b). Column temperature, 80°.

The apparatus shown in Figs. 3 and 4 is easy to assemble and to adapt to field sampling. It should be considered, however, as a prototype only. For practical use, the dimension and content of the cartridge, the flow rates, and a variety of other parameters should be optimized.

The two-cartridge approach (Fig. 2) proved valuable in defining the characteristics of sampling. Fig. 5 shows a chromatogram of gasoline, the original multi-component test mixture, on a packed GLC column. It is obvious that a capillary would have offered much better resolution, but our exploratory studies were well served by this simple arrangement. Figs. 6 through 8 show the results of typical experiments sampling gasoline and car exhaust. The analysis of the second cartridge conforms to expectations and shows the point of complete retention in the first cartridge to occur at a Kováts index of about 1000.

The extracts of car exhaust from the cartridges proved well suited for different types of analysis such as coupled GC–MS, and the use of various selective detectors such as flame photometric, alkali flame, and electron capture. Fig. 9 points to some of the advantages of a dual detector system in identification studies. Although there is nothing new about these approaches, they are mentioned here to demonstrate the compatibility of the described air sampling method with various analytical techniques.

In atmospheric sampling, no particular attention was devoted to the question of relative collected amounts. Not only does the organic content of the atmosphere vary with the weather and the traffic, but the ambient temperature, the content and pressure drop of the cartridge, and a multitude of other parameters can determine how much is actually collected. The case of car-exhaust sampling is similar.

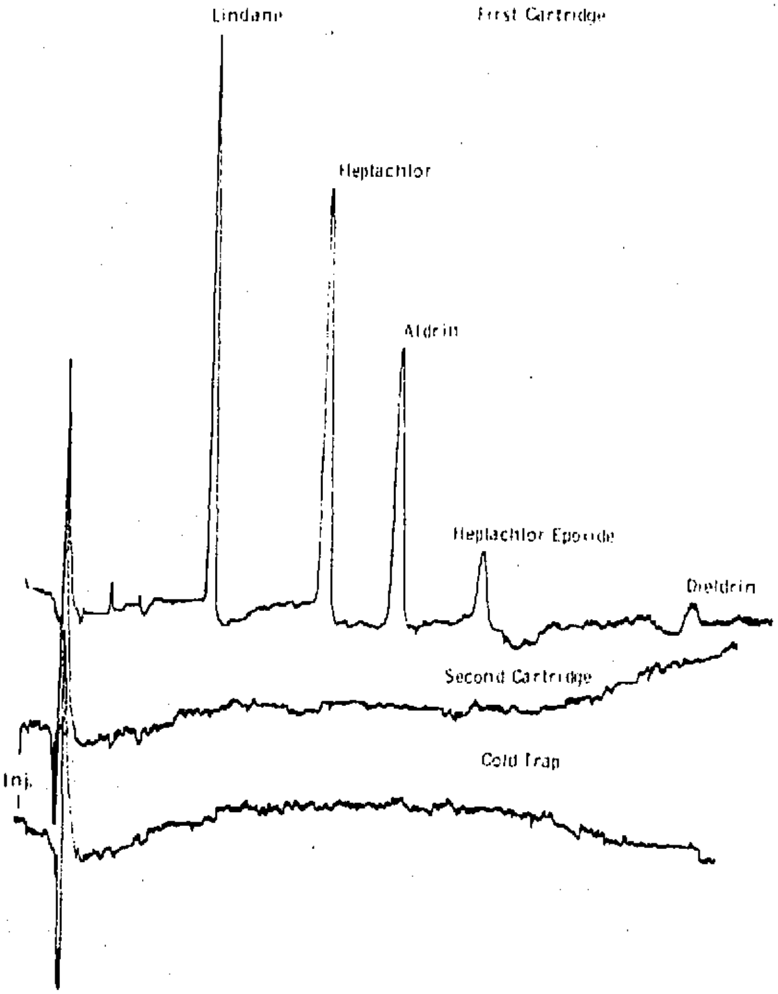

Fig. 10. Electron capture gas chromatograms of chlorinated hydrocarbon insecticides collected from a doped air stream by two cartridges containing 24% $(C_{18}H_{37}SiO_{3/2})_n$ on Chromosorb A, 20/30 mesh and 31% $(C_{18}H_{37}SiO_{3/2})_n$ on Diatom W, 20/40 mesh. Sampling rate, 18 l/min; sampling time, 120 min.

There, as in the study of chlorinated hydrocarbon insecticides (Fig. 10), we assumed that quantitative retention of a particular compound in the first cartridge was indicated by its absence in the second cartridge. In the case of the insecticides, an

Fig. 11

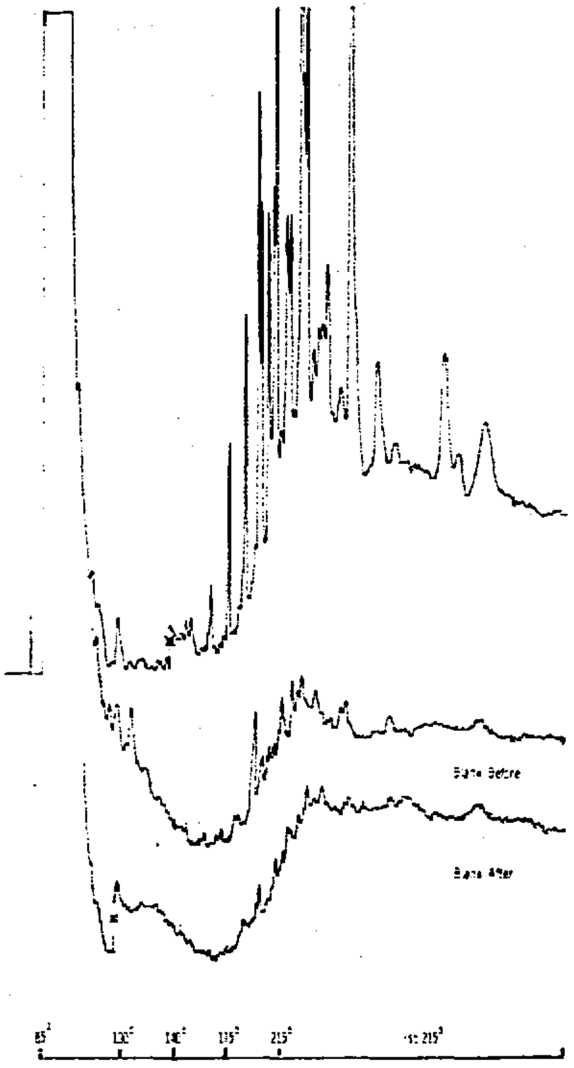

Fig. 12

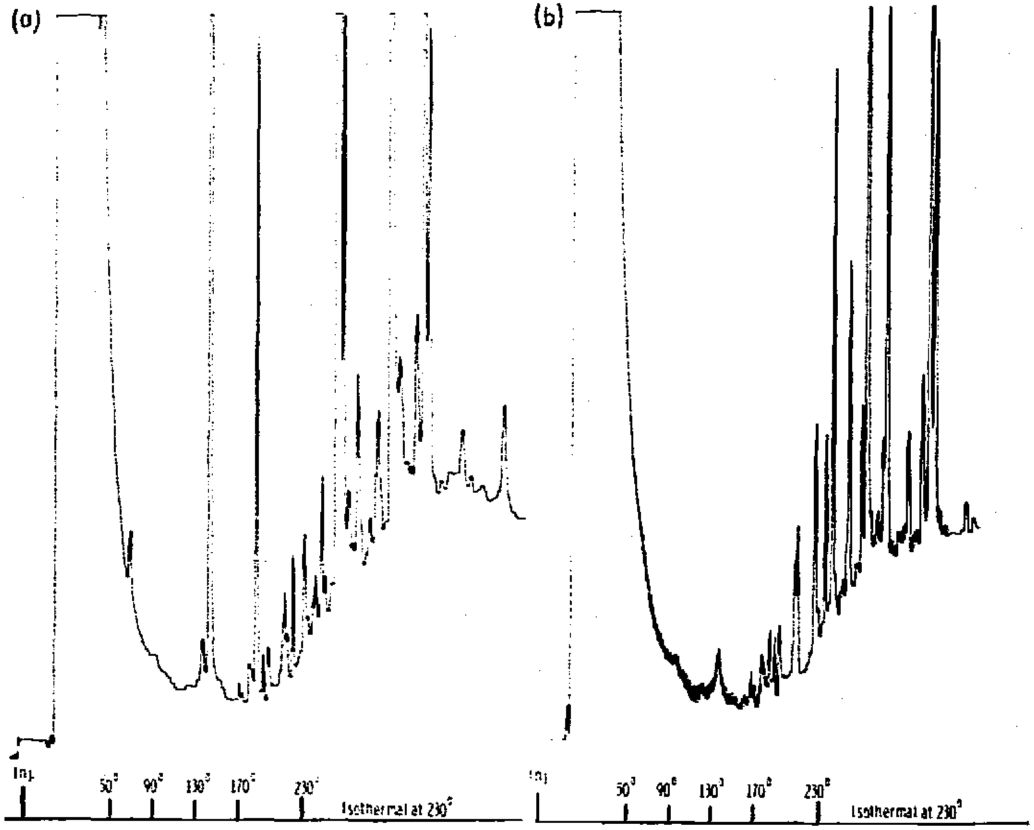

Fig. 11. Gas chromatograms of extracts from a single cartridge containing 26% $(C_{18}H_{37}SiO_{3/2})_n$ on Chromosorb W, 30/60 mesh, used in an early sampling experiment of Columbia campus air in the vicinity of a road being tarred. Sampling rate, 10 l/min; sampling time, 3:00 p.m. to 8:00 p.m. the next day. The injection represents *ca.* 4 l of air. GC conditions: 10% OV-17 on Chromosorb W-HP, 80/100 mesh, 6 ft. × 3 mm I.D. Pyrex; nitrogen flow, 33 ml/min, FID.

Fig. 12. Gas chromatograms of organics collected from two areas in St. Louis by 14% $(C_{18}H_{37}SiO_{3/2})_n$ on Chromosorb G, 45/60 mesh. Sampling rates *ca.* 18 l/min, sampling times *ca.* 10:30 a.m. to 5:30 p.m. The injections represent *ca.* 20 to 30 l of air. GC conditions as in Fig. 5.

additional cold trap was used. Due to their low vapor pressure, the quantitative retention of these chlorinated hydrocarbons in the first cartridge was predictable.

Finally, Figs. 11 and 12 show typical examples of atmospheric sampling. An identification of the collected compounds was considered beyond the scope of this exploratory investigation; however, the described techniques should hopefully lead to just such studies of identification.

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