

CHROM. 6219

THE USE OF SUPPORT-BONDED SILICONES FOR THE EXTRACTION OF ORGANOCHLORINES OF INTEREST FROM WATER*

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(Received May 8th, 1972)

SUMMARY

Water was spiked with various types of chlorinated organics at trace levels, in an effort to demonstrate the potential of support-bonded silicones to collect these pollutants from natural aqueous systems. Greater amounts of the spiked water were pumped through a bed of a silicone phase, followed by a small amount of pentane. The pentane eluted the collected organochlorines, ready for determination by electron capture gas chromatography. This approach proved successful for most model compounds at parts per trillion levels.

INTRODUCTION

For several years now, considerable public and scientific attention has been focused on the occurrence of trace amounts of organochlorine insecticides and related compounds in natural water systems. Various attempts were undertaken to develop more sensitive (and less expensive and time-consuming) techniques for the initial collection. An extensively used method is the adsorption on, and subsequent desorption from, activated carbon^{1,2}. The second widely-used method is liquid extraction, either in batchwise³⁻⁵ or continuous⁶ manner. A valuable literature source for developments in this area are the biannual *Analytical Chemistry Reviews*^{7,8}; and HERZEL's paper⁹ on a fast method for organochlorine insecticides contains a good literature section.

The application of reversed-phase partition in pesticide analysis, using porous polymer particles as stationary phases, has been suggested^{10,11}. This approach has, incidentally, proven quite successful for the extraction of various (non-halogenated) organics from water¹². Recently, AHLING AND JENSEN¹³ employed reversed-phase liquid-liquid partition to collect chlorinated hydrocarbons and polychlorinated biphenyls from water with amazing sensitivity (10 ng/m³ or 10 p.p.q. of lindane). A mixture of *n*-undecane and Carbowax 4000 monostearate on Chromosorb W

* Contribution from the Missouri Agriculture Experiment Station, Journal Series No. 6400. Supported by a grant from the Rockefeller Foundation, NSF Grant GP-18616, and the Environmental Trace Substances Center, Columbia Mo., U.S.A.

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served as the collection medium. Reported recoveries ranged from 50 to 100% of the pesticides added to water.

Our study involved the use of support-bonded silicones¹⁴⁻¹⁶ for the initial extraction. These materials—thick films of silicones which are chemically bonded to diatomaceous earth particles, consequently unextractable by organic solvents—were suspected to be capable of extracting non-polar organics from aqueous systems. Subsequent recovery was envisioned by elution with pentane, which an earlier study¹⁷ had shown to be effective for this purpose.

The potential use of support-bonded silicones held some interest for us, mainly because of the simplicity of approach: the collection medium could be used over and over; no cumbersome concentration of solvents was anticipated; and we expected a minimum of decomposition of the organochlorines to occur on the absorbent phase.

EXPERIMENTAL

Surface-bonded $[C_{18}H_{37}SiO_{3/2}]_n$ on 40-60 mesh Chromosorb G was prepared as described earlier¹⁴. Repeated extractions with methanol and benzene in both Soxhlet and Goldfish set-ups served to remove any traces of non-surface-bonded phase.

About 7 g of this material (which contained 13 % silicone polymer as determined by ignition analysis) were filled between glass wool plugs into a 35 × 1 cm I. D. glass column with 6 mm O. D. terminals. The column inlet was connected via Swagelock fittings (with PTFE ferrules) to a 3 mm O.D. PTFE tube whose other end was submerged in the water sample.

The column outlet was connected in similar fashion to a large suction flask and, in turn, to a water aspirator. Scrupulous cleaning of the glassware was anticipated and found to be necessary.

In a large glass reservoir, 10 l of stirred water were doped with the organochlorines dissolved in 0.1 ml of acetone. The stirring was continued for 45 min; then the Teflon inlet tube was hung into the water and the water aspirator maintained a flow of about 50-55 ml/min through the collection column.

After sampling, the column was dried with pure nitrogen and the organochlorines eluted with two 5-ml portions of "Nanograde" pentane by gravity flow. The pentane extracts were injected directly onto a 170 cm × 3.5 mm I.D. Pyrex column, packed with 1.5 % QF-1 + 2.0 % OV-17 on 100-120 mesh Chromosorb W HP, at a nitrogen flow of *ca.* 60 ml/min. The injection port temperature of the MT-220 gas chromatograph was kept at 225°, the temperature of the ⁶³Ni electron capture detector at 275°. Standards containing the organochlorines in concentration as expected from 100 % recovery were run in immediate succession, as shown in Figs 1-3.

In addition, Columbia tap water and a grab sample from the Missouri river were run. The latter was filtered through a 5- μ Millipore PTFE filter and centrifuged to remove any particulate matter.

RESULTS AND DISCUSSION

This study was designed to explore and demonstrate the potential application of support-bonded silicones to extract chlorinated organics from water at trace levels.

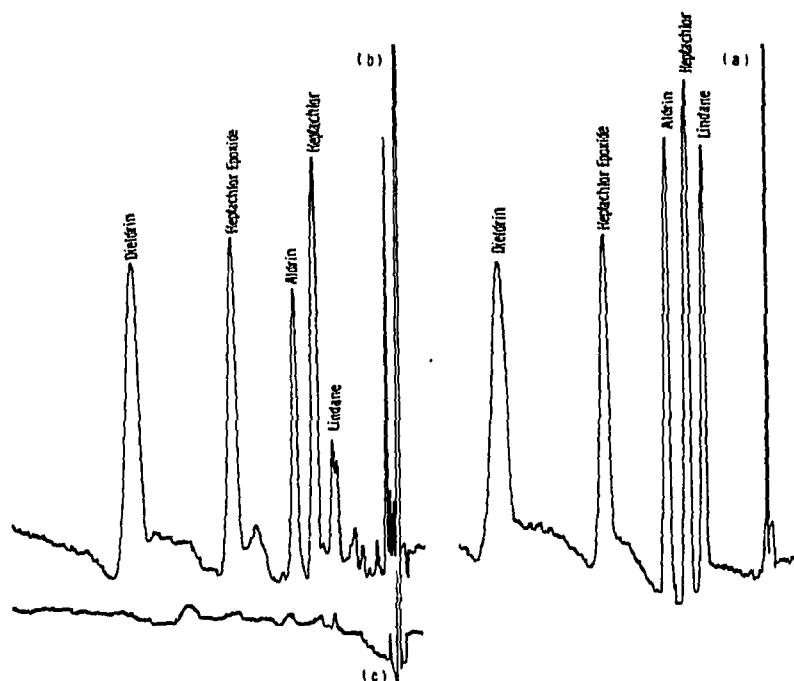


Fig. 1. Recovery of chlorinated hydrocarbon insecticides. (a) Standards injected (pg): Lindane, 100; heptachlor, 150; aldrin, 120; heptachlorepoiside, 200; dieldrin, 200. (b) Standards recovered in first pentane fraction from water spiked with the following p.p.t. (10^{-12} , w/v) levels: Lindane, 10; heptachlor, 15; aldrin, 12; heptachlorepoiside, 20; dieldrin, 20. (c) Second pentane fraction. GC column temperature: 185° .

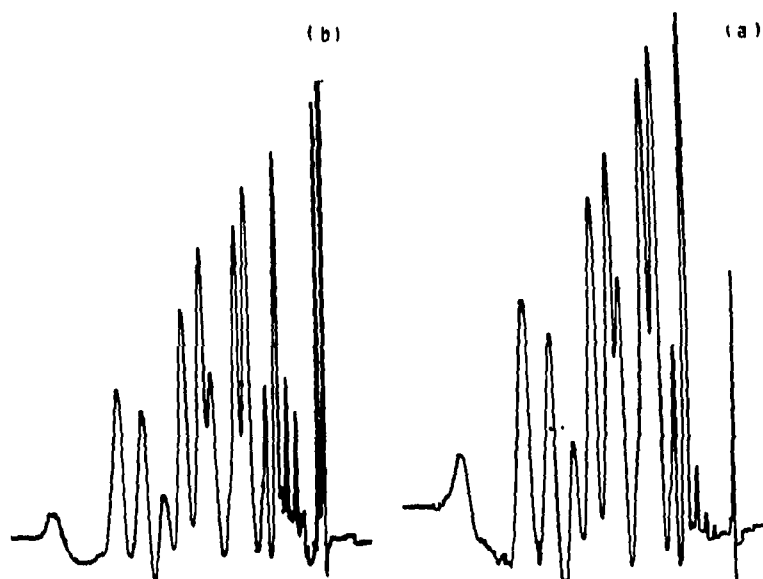


Fig. 2. Recovery of polychlorinated biphenyls. (a) Standard injected: 2.5 ng Aroclor 1254. (b) Standard recovered in first pentane fraction from water spiked with 250 p.p.t. of Aroclor 1254. GC column temperature: 197° .

It was to investigate an approach which could conceivably avert the major impediments to the two established methods of analysis: The decomposition or irreversible adsorption caused by activated carbon; and the procedural and chemical difficulties posed by the large volumes of solvents usually employed for extraction.

The demonstration of applicability is shown in Figs. 1-3. The collection of

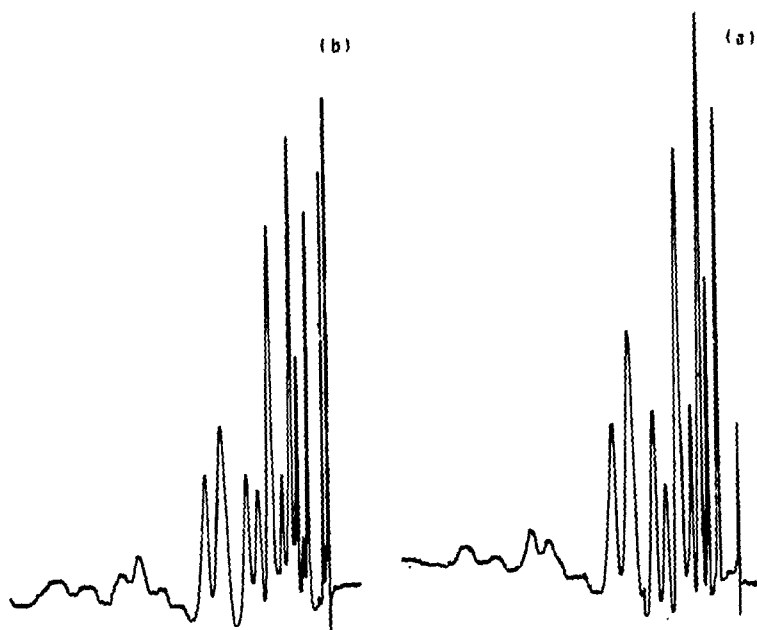


Fig. 3. Recovery of polychlorinated naphthalenes. (a) Standard injected: 2 ng Halowax 1013 (b) Standard recovered in first pentane fraction from water spiked with 200 p.p.t. Halowax 1013. GC column temperature: 197 °.

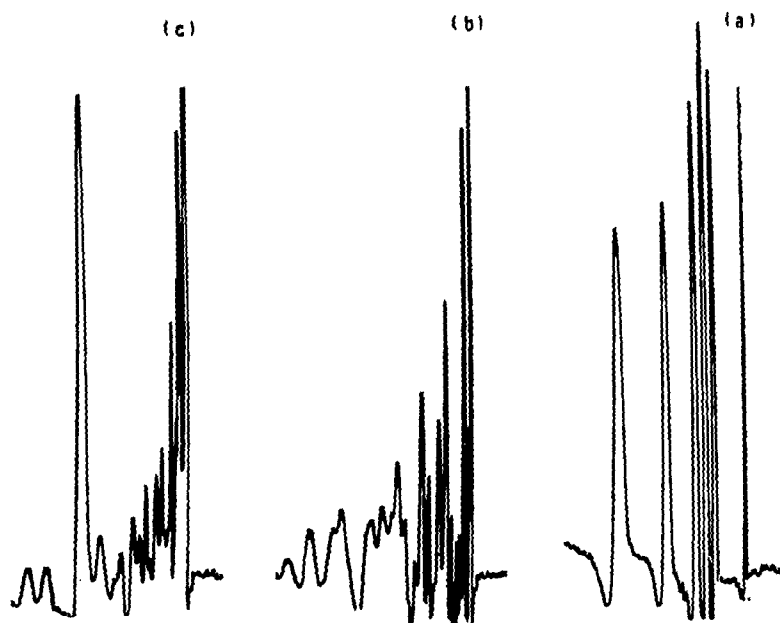


Fig. 4. Extraction of compounds from water samples (a) Standard chlorinated hydrocarbons in order of elution: Lindane, heptachlor, aldrin, heptachlorepoide and dieldrin. (b) Filtered Missouri river water; 2-l original sample. (c) University of Missouri (Columbia) tap water; 10-l original sample. GC column temperature: 195 °.

organochlorines in the p.p.t. range proved generally successful, although some poor recoveries, *e.g.* that of lindane, were evident. We kept the approach simple: Spiked water was pumped through a column, the column dried with nitrogen, and the spikes eluted with a small amount of pentane for direct injection into the gas chromatograph. The elution was essentially complete and subsequent pentane fractions contained at most traces of organochlorines.

Yet, several questions remain to be answered. We did not investigate the types of chemical compounds which the method would embrace. Presumably non-polar organics are retained while polar ones may pass through the column. Better retention could probably be achieved by higher loads of the support-bonded silicone film or by the use of chemically different polysiloxanes. The amount of the collection medium and its geometrical configuration, *i.e.* the volume and the length/I. D. ratio of the column, would need to be optimized to meet particular analytical objectives.

The "analysis" of filtered Missouri river water (Fig. 4) illustrates a further point of interest. This chromatogram would be worthless, for instance, for the analyst interested in the pesticide content of this large and exceedingly turbid stream, unless the suspended matter were analyzed separately (compare, for instance, refs. 18 and 19). However, introducing the particulates onto the column would have amounted to a zone of soil on its top, which could have been expected to release adsorbed organics only slowly to large portions of pentane.

The object of the "analysis" of Missouri water, obviously, was not knowledge on the river's pesticide burden, but some conception of how much truly dissolved material would give rise to signals from the electron capture detector. This "background" level proved quite low, a rather welcome finding. The other analysis of a water sample, shown in Fig. 4, was run for personal interest. The chemical nature of the large peak originating from Columbia tap water, however, was not further investigated.

In summary, support-bonded silicones appear good candidates for use in fast and sensitive analytical methods designed to determine dissolved organochlorines in water.

NOTE ADDED IN PROOF

While this manuscript was in print, we became aware of the work of two groups^{20,21} who use polymers as collection media for chlorinated hydrocarbons, and who should have been included in the short literature review.

ACKNOWLEDGEMENTS

We thank Drs. D. L. STALLING and J. WAGSTAFF for donations of Aroclor and Halowax; and Dr. R. F. MOSEMAN for competent assistance in gas chromatography.

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