Analysis of Pesticides in Water Using Silica Gel Column Clean-up

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In developing a program for monitoring pesticides in river waters in Iowa it was necessary to develop methodology which was both accurate and relatively non-time consuming. Since samples were to be collected from a number of Iowa rivers which sometimes contain levels of organic compounds that interfere with the electron capture gas chromatography of the low levels of pesticides present, a simple clean-up step with quantitative recovery was required. The silica gel column clean-up step described in this paper is simple, rapid and gives complete recovery of the pesticides being determined.

Procedure

Samples are collected on site in quart glass jars with teflon lid liners and mailed to the laboratory in polystyrene cartons. The samples are extracted by the procedure of Kawahara (1) with 50 ml of petroleum ether.

The extract is concentrated to approximately 1 ml using a miniature Kuderna-Danish apparatus (Figure 1). This consists of a 15 ml graduated, glass-stoppered ₹13 centrifuge tube, a 100 ml volumetric flask with the neck shortened and a male ₹13 joint attached to the bottom and a Vigreux column made from a male flask length ₹13 joint. A commercially available ebullator (Kontes of Illinois, Franklin Park, Illinois) is added to the centrifuge tube. A heater block similar to the design of Beroza and Bowman (2) is used as a heat source for the miniature Kuderna-Danish. This concentrating device can be left unattended for hours without going dry and with virtually no loss of pesticides.

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Silica gel, 60-200 mesh chromatographic grade 950 (Fisher Scientific Co.), is deactivated by the addition of 1% by weight distilled water and stored in a tightly capped bottle. It should be well mixed and stored 24 hours before use.

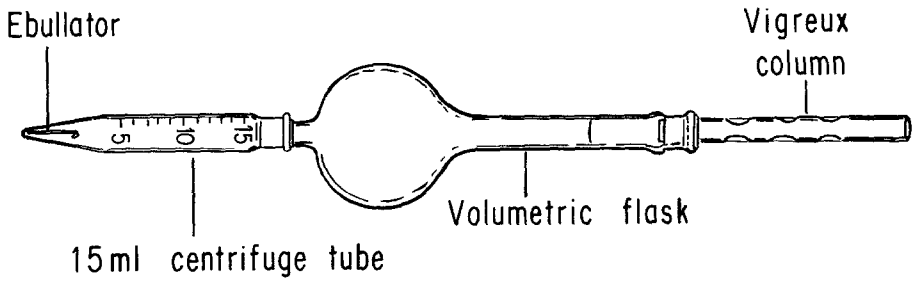

Figure 1

The tip of a chromatographic column with a 6 mm I.D. and a reservoir on top is plugged with glass wool and 1 gram of the deactivated silica gel is added. Pre-wet the column with 5 ml pesticide grade hexane. When the top of the hexane reaches the silica gel, place a calibrated 15 ml tube under the column and transfer the concentrated extract onto the silica gel with a pipette. Rinse the tube which contained the extract with ½ ml of hexane and add this to the chromatographic column. When the top of the hexane reaches the silica gel carefully add 6.5 ml of 10% by volume benzene in hexane. After this solvent has reached the surface of the silica gel place another calibrated tube under the column and add 6.5 ml of 60% by volume benzene in hexane to the column.

The two fractions collected from the column by this procedure will contain the chlorinated hydrocarbon insecticides. They are concentrated to the desired volume with a gentle stream of filtered air and a suitable aliquot is injected into a gas chromatograph equipped with an electron capture detector for qualitative and quantitative analysis.

Figure 2 shows a gas chromatographic analysis of a standard pesticide mixture (A) and the two fractions (B, 10% benzene elute--C, 60% benzene elute) obtained by applying the silica gel column clean-up detailed in this procedure to this standard pesticide mixture. The samples were run on an F & M model 400 gas chromatograph with an electron capture detector. A 3 mm I.D., 4 ft. long, glass column with a mixed 3%:2% QF-1:OV-1 polar phase was used for the analysis.

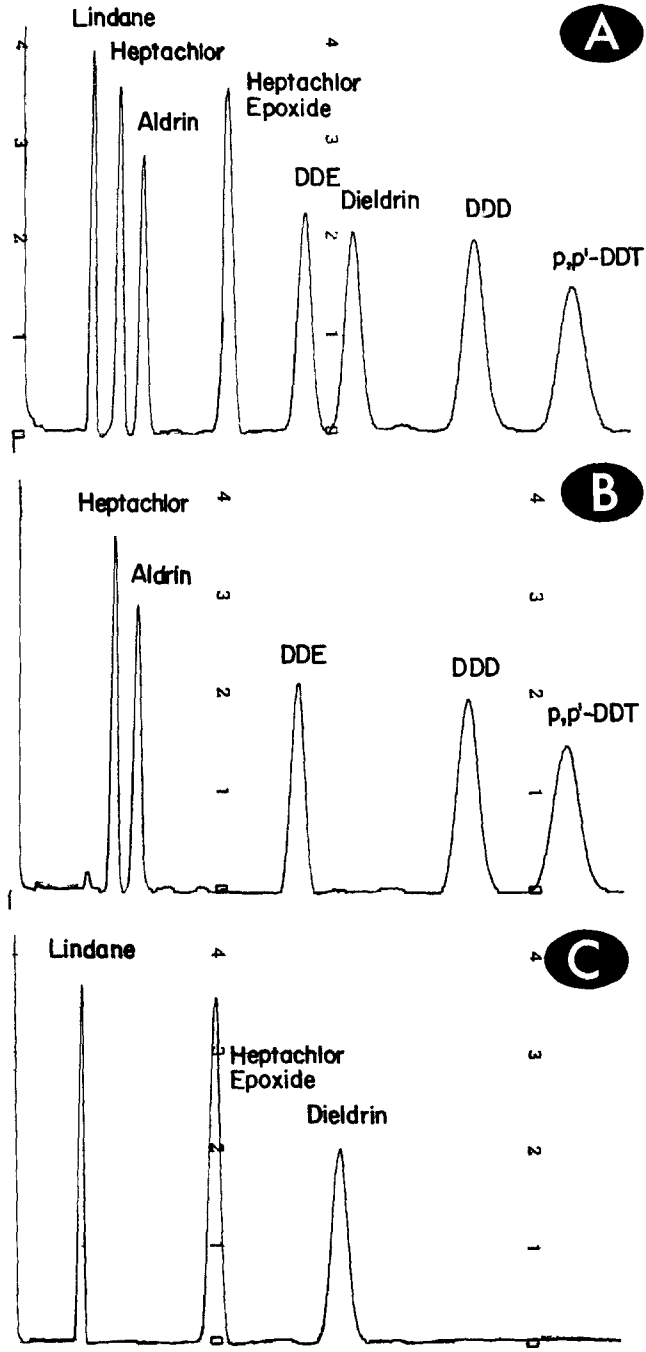

Figure 2

A Standard pesticide mixture
B 10% fraction of A from 1 gram silica gel column
C 60% fraction of A from 1 gram silica gel column

Discussion

The advantage of the extraction and concentration steps used in this procedure is the ability to process a large number of samples with a minimum of actual work time.

The 1 gram silica gel column used has sufficient adsorptive capacity to clean-up a one quart water sample. Because of the small amounts of the adsorbant and solvents used, the trace amounts of pesticides in a quart water sample can be quantitatively recovered without contamination by artifacts from the reagents or loses from concentrating large volumes to the necessary small final volumes.

The activity of the 1% deactivated silica gel is extremely stable. The batch used for the preparation of the samples shown in figure 2 was prepared approximately six months earlier and used routinely without any change in its characteristic separation of the pesticides.

The separation of the commonly occurring heptachlor epoxide into the second (60%) fraction gives additional confirmation to its identification by separating it from other less polar chlorinated compounds which would occur in the first (10%) fraction.

More polar compounds, such as organophosphorous insecticides, which are retained on the silica in this procedure can be eluted in a third fraction by the use of a more polar solvent system such as 10% by volume ethyl acetate in benzene.

The method presented here has proven satisfactory for the routine monitoring of water samples containing chlorinated hydrocarbon pesticides in low parts per trillion concentrations.

REFERENCES

1. F K Kawahara, J W Eichelberger, B H Reid and H Stierli, Jour Water Poll Control Fed, 39, 572, (1967)

2. M Beroza, M C Bowman, Anal Chem, 39, 1200, (1967)