

Identification of the Aldrin Artifact

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Electron-capture gas chromatography is not specific for organochlorine pesticides. A material which behaves like aldrin when chromatographed on a DC-200 column or QF-1-DC-200 mixed column has been found in reagents and soil samples and

identified by x-ray emission spectroscopy as elemental sulfur. Suggestions for its removal from reagents and the handling of samples containing it are included.

One of the most popular detectors for gas-liquid chromatography (GLC) of pesticides is the electron-capture (EC) detector, because it is very sensitive and relatively specific. Since this detector is not entirely specific for pesticides, many laboratories employ a second method, such as microcoulometry, to assist in identification of the pesticides. A silver cell is used for chlorine-containing pesticides and a platinum cell for those containing sulfur.

Because of the sensitivity of the electron-capture detector, reagents used in the preparation of the sample must be free from materials which give interfering peaks on GLC-EC. Lee *et al.* (1966) have reported an artifact in reagents which behaves as BHC or aldrin during GLC-EC and identified it as di-*n*-butyl phthalate. Sans (1967) also reported spurious responses in reagents. We have found a material in anhydrous sodium sulfate, Florisil, and hexane which behaved similar to aldrin on GLC-EC. The quantity of this material varied among lots of the same reagent and, in contrast to the findings of Lee *et al.* (1966), simple distillation did not remove the artifact. However, refluxing over bright metallic sodium yielded hexane that was more suitable for GLC-EC than the highly purified product obtained commercially. This interfering material was also present on cleaned glassware, regardless of the detergent used for cleaning.

During routine determinations of chlorinated hydrocarbon pesticides in soils, a sample was encountered which contained enormous quantities of material which behaved in the same manner as the aldrin-like material found in our reagents. A sufficient quantity was obtained by crystallization. Its identification is the subject of this paper.

EXPERIMENTAL

All gas-liquid chromatography was carried out on Micro-Tek gas chromatograph, Model MT-220. Coulometry was done with a Dohrmann microcoulometer Model C-200. The chromatograph columns were 6-foot \times $\frac{1}{4}$ -inch O.D. glass U-tubes filled with equal parts of 13% QF-1 on Gas Chrom Q and 8% DC-200 on Gas Chrom Q or with 10% DC-200 on Anakrom ABS. The column oven was operated at 190° C. and the EC detector at 200° C. The nitrogen carrier gas flow was 150 cc. per minute. Under these conditions, aldrin eluted in 3.0 and 2.7 minutes, respectively. These columns were used

because they represent two types of columns currently in use in the pesticide residue field.

Ten grams of soil was placed in a washed extraction thimble and extracted under reflux with acetone-hexane (1:1) for 4 hours. The extract was concentrated under vacuum and transferred to a column made of 30 grams of aluminum oxide (Merck) previously deactivated with 10% water. One hundred milliliters of hexane served for elution. The eluate was concentrated under vacuum and transferred to a Florisil (Floridin Co.) column. Four hundred milliliters of 15% ethyl ether (containing 2% ethanol)-85% hexane was used for elution. The eluate was concentrated under vacuum for GLC-EC analysis. These two column fractionation steps are required to clean the soil extracts sufficiently for analysis. It appears that impurities not removed by one column are removed by the other.

RESULTS

When the Florisil eluate was concentrated, crystals formed in the flask. They were filtered off and recrystallized from hexane. Formation of crystals from a Florisil eluate is highly unusual.

A sample of these crystals was dissolved in hexane and subjected to gas-liquid chromatography, using the electron-capture detector and both the chlorine and sulfur titration cells on the microcoulometer. On GLC-EC, the material gave three peaks with retention times relative to aldrin similar to those obtained for pure sulfur (Figure 1). The solution was diluted so that a measurement could be made on the largest peak. No response was obtained on the microcoulometer chlorine titration cell. Responses obtained on the sulfur titration cell are very close to those obtained for pure sulfur (Figure 1). Retention times given for the sulfur titration cell are relative to sulfenone.

A sample of the recrystallized material melted at 114-116° C. on a Köfler micro-melting point hot stage. The melting point for pure sulfur varies from 106° to 119° C. (Heinrich *et al.*, 1961), depending on the crystalline form and the speed of heating. Another sample of the crystals was subjected to x-ray emission spectroscopy. The observed angle of the reflected x-rays (2θ) was 144.6°. The wavelength of this reflected beam was calculated as 5.372 Å. from Bragg's formula. The wavelength for the $K\alpha$ transition for sulfur is 5.373 Å. (Powers, 1957).

DISCUSSION

The identity of the material having an aldrin-like response on GLC-EC has been established as elemental

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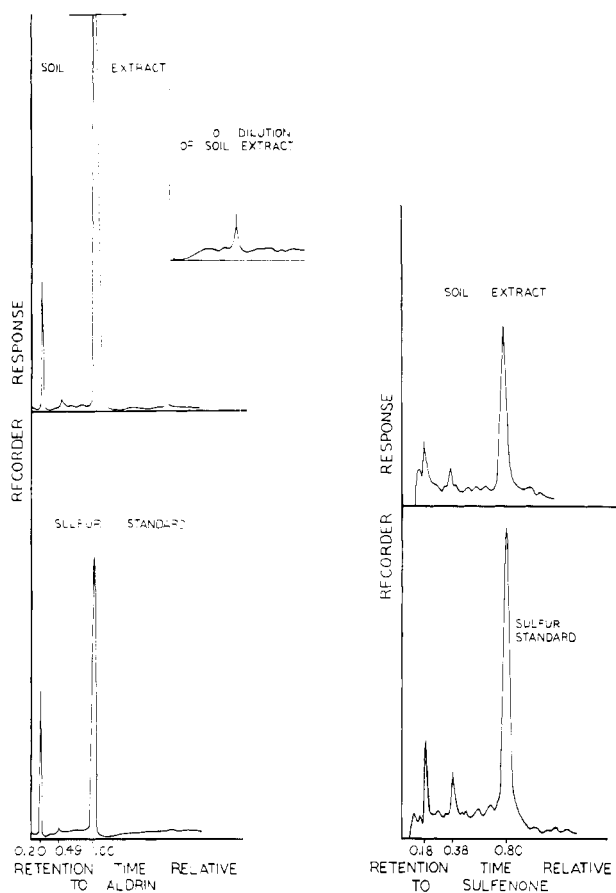


Figure 1. Behavior of sulfur on GLC

Chromatograms on the left were obtained when the respective materials were injected on the 13% QF-1-8% DC-200 column and the column effluent monitored with an electron-capture detector. Other chromatograms resulted from injection of the samples on the 10% DC-200 column and monitoring the column effluent with the microcoulometer sulfur titration cell. Aldrin would have a retention time relative to sulfenone of 0.80 on the latter column if the chlorine cell had been used

sulfur. The specifications for free sulfur in some of the reagents currently used is not in disagreement with this finding. Three forms of sulfur may be present to give the three peaks on GLC-EC. The peak occurring near aldrin is the largest and that near BHC is the smallest. The two smaller peaks usually are not seen because of dilution of the sample before injection.

Sulfur is widely used as a fungicide and thus it is not surprising to find large quantities in some soil samples from agricultural areas. However, if it is present, neither aldrin nor BHC can be determined accurately by GLC-EC unless some additional procedure is carried out, such as that suggested by Sans (1967). Indication that such an additional procedure is required would be a positive response at the retention time for BHC or aldrin with the microcoulometer chlorine titration cell.

A practical solution to the problem of impure reagents in our laboratory has been to purchase commercial "85% purity" hexane in large quantities and distill it over bright metallic sodium. (Note. Sodium is very reactive and due caution must be exercised in its use with a flammable solvent such as hexane.) Preshipment samples of Florisil and anhydrous sodium sulfate are obtained and analyzed before purchase is made. All glassware is rinsed thoroughly with redistilled hexane before use. Soil samples which appear to contain aldrin are subjected to critical microcoulometric analysis and if aldrin still is suspected, further steps are taken to verify its presence.

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