

Purification Procedure for Low Polarity Solvents

A method is described for producing highly purified solvents for use in pesticide residue analysis by GLC, particularly when an electron-capture detector is employed. The method consists of a sulfuric acid wash, a strongly alkaline permanganate reflux, and distillation. The solvents prepared by this

method (when concentrated 100 to 1) gave narrow solvent peaks and no later eluting peaks upon gas chromatographic analysis. In both respects, the solvents prepared by this method were superior to commercially available pesticide grade solvents.

The high sensitivity of gas chromatographic detectors to some high-boiling contaminants which are present in the usual ACS grade solvents has made necessary the use of specially purified materials. These contaminants appear in the chromatogram as excessively broad solvent peaks with later eluting peaks which may interfere with determination of the compounds of interest.

Most authors report the use of carefully distilled solvents in pesticide analysis. Generally the solvents have been distilled in glass equipment in the laboratory (Clark *et al.*, 1967; Howard *et al.*, 1966; McLeod *et al.*, 1967; Mills *et al.*, 1963), or purchased from commercial suppliers (Chiba and Morley, 1968; Kadoum, 1967; Storherr *et al.*, 1967).

Other techniques of solvent preparation have been developed for use in such applications as fluorimetry, spectrophotometry, and other analytical methods. Absorption chromatography (Howard *et al.*, 1966; Perrin *et al.*, 1966), sulfuric acid and acidic permanganate washing (Fieser, 1957; Perrin *et al.*, 1966), or alkaline permanganate washing (Perrin *et al.*, 1966) have been suggested as solvent purification techniques.

In most analyses, the commercial "pesticide grade" material is quite satisfactory. Occasionally, however, it is necessary to determine very low concentrations of pesticides—e.g., water samples. In analyses of this type, it is often necessary to concentrate a large volume of solvent prior to injection with no intervening cleanup step. This procedure frequently produces interferences which would be insignificant in the usual residue procedures and pose a problem only because such small traces of pesticides are of interest. The purpose of the work reported here was to develop a technique for producing sufficiently pure solvents for use in these special applications.

MATERIALS AND METHODS

The solvent was first washed with concentrated sulfuric acid to remove gross impurities. This was easily accomplished in the case of aliphatic hydrocarbons by allowing the solvent to stand over the acid for a period of several days. In the case of benzene, the solvent was shaken with the acid in a large separatory funnel (100 ml. of acid with 4 liters of benzene). The solvent was then washed with distilled water to remove most of the acid, and transferred to a 5000-ml. three-neck distillation flask. The solvent was then refluxed with 100 grams of NaOH pellets in 200 ml. of water. The mixture was vigorously stirred with a Teflon blade-stirrer to ensure good contact with the aqueous phase. After 30 minutes, a small amount of KMnO_4 (2 to 3 grams) was added through the condenser (NOTE: The addition of permanganate must be done very carefully to prevent dangerously rapid boiling of the solvent). When the permanganate is nearly decolorized, more was added until 30 grams had been introduced over a 1½-hour period. The mixture was then allowed to reflux for an additional 30 minutes. Stirring was continued until the mixture had cooled to room temperature.

The top layer was then decanted into a distillation flask which was fitted with a Hempel-type distilling column (Corning 92010) with 4.5-mm. glass helices packing (Kontes K-509250). Partially crushed NaOH pellets (100 grams) were then added, and the mixture was allowed to stand overnight. The solvent was then distilled with a 3-to-1 reflux ratio. The first 200 ml. was discarded and the next 2000 ml. was collected as product. Further collection resulted in broadening of the solvent peak.

RESULTS AND DISCUSSION

Figure 1 illustrates typical chromatograms obtained when hexane in various stages of purity was concentrated 100-fold

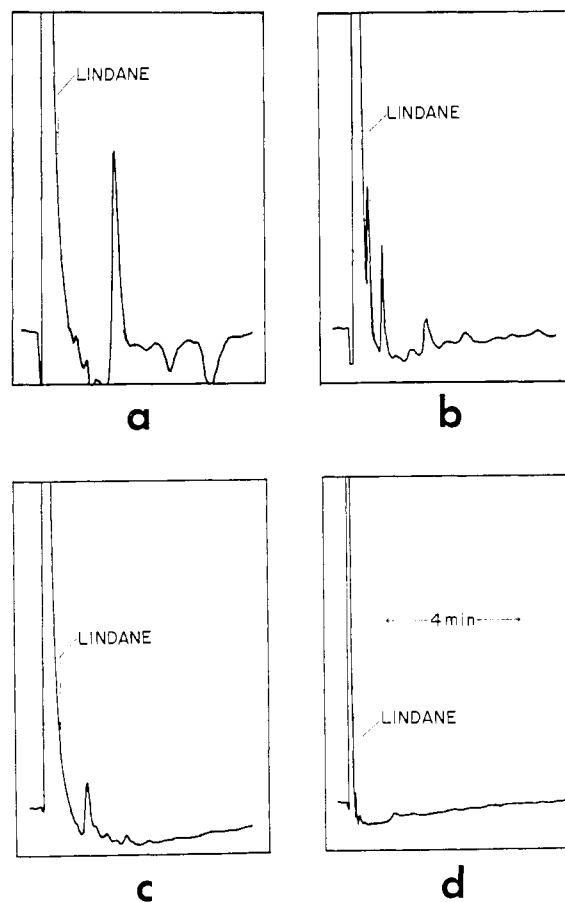


Figure 1. Electron-capture chromatograms of various grades of hexane

- ACS grade as received
- acid washed
- commercial "pesticide grade"
- hexane prepared by the described method

The chromatograms shown resulted from 4- μl . aliquots of each solution under identical conditions. Each type of solvent was concentrated 100 to 1 by use of a filtered stream of high purity nitrogen and a warm (50° C.) water bath. Chromatographic conditions are given in the text

and analyzed with the gas chromatograph. Chromatogram **a** illustrates ACS grade hexane which has received no further treatment. The solvent peak was quite wide and numerous later eluting peaks appear (many of these were negative-going, which suggests that they were caused by high concentrations of high-boiling materials). Chromatogram **b** illustrates hexane which has been washed twice with concentrated sulfuric acid, rinsed with distilled water, and dried with anhydrous sodium sulfate. Improvement is apparent; however, the solvent peak is still broad and some later eluting peaks appear. Distillation of this material gives a product comparable, or slightly better, than the commercial "pesticide grade" which is illustrated in chromatogram **c**. Chromatogram **d** was obtained with the product from the described procedure. GLC conditions were the same in all chromatograms, and were as follows:

Column. 1.6 meter \times 3 mm. I.D. coiled borosilicate glass packed with 0.15% DC 710 on 80- to 100-mesh Corning 0201 glass beads.

Column temperature. 165° C.

Carrier (N₂) flow. 35 ml. per minute.

Sensitivity. 1×10^{-10} AFS.

The retention time of lindane is shown for reference purposes.

The method described was used for the preparation of hexane, petroleum ether, isooctane, and benzene. In each case, the chromatogram obtained from analysis of the solvent, after concentration, showed a narrow solvent peak with no

later eluting peaks of greater than 0.05% of full scale. Under the analytical conditions used, 60 picograms of lindane gave 50% scale deflection.

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