Forced Volatilization or Sweep Extraction of Organochlorine Pesticide from Vegetable Extracts

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The sensitivity of the electron capture detector to numerous natural products requires a good cleanup of vegetable extracts when this type of detector is used for organochlorine pesticide residue analysis (1).

OTT and GUNTHER (2) achieved some partition by the forced volatilization with nitrogen of organochlorine pesticides from butterfat and alfalfa (3), followed by gas chromatographic analysis with the Dohrmann microcoulometric detector. More recently, STORHERR and WATTS (4) used an equivalent cleanup procedure to separate organophosphate pesticides from vegetable extracts; they analyzed the residues by gas chromatography with a sodium thermionic detector.

We proposed to get sufficient cleanup to analyze organochlorine pesticide residues by gas chromatography using an electron capture detector in a similar way (1).

VOLATILIZATION CLEANUP APPARATUS

The apparatus for cleanup (Fig. 1) is similar to that of GUNTHER et al. (3) and consists of an electric furnace for microanalysis with an alternostat selector of temperature. This

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cylindrical furnace a (22 cm. long, 1.8 cm. I.D.) admits a large borosilicate tube b (23 cm. long, 1.6 cm. O.D.) that ends with a male ₮ joint. A Teflon sleeve joins it to the female joint of the

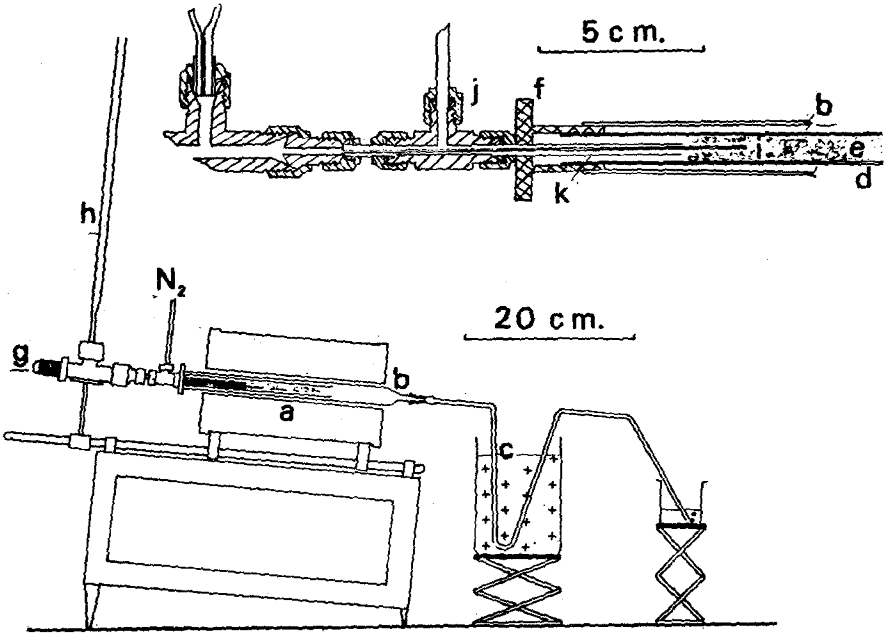

Fig. 1. Forced volatilization or sweep extraction apparatus. See text for details.

bubbling tube c. This is bent as shown, is surrounded with ice in the large beaker, and terminates in a small beaker containing petroleum ether. A small borosilicate tube d (17 cm. long, 1.0 cm. O. D.) set inside the large tube b contains 0.2 g. of borosilicate wool e renewed for every cleanup.

A Teflon stopper f joins the large tube and the inside tube to the metal solvent and nitrogen entrance structure. This structure includes: a micrometer valve g (1/4") for regulation of the flow of petroleum ether. This valve receives a vertical glass tube h which serves as a solvent tank of 10 ml. capacity. A Teflon sleeve protects and seals the joint. The petroleum ether flows from the valve and reaches the borosilicate wool through a stainless steel pipe i (1.5 mm. O.D.). This pipe goes through a T-joint j (1/8") which allows entrance of the nitrogen. Nitrogen arrives at the borosilicate wool through a stainless steel pipe k (3.1 mm. O.D., or 1/8") that encases the solvent pipe i. This structure allows separate regulation of solvent flow and nitrogen flow.

METHOD

The vegetable sample is extracted, for instance by acetonitrile; the residue in the acetonitrile is then partitioned into petroleum ether (1), and the ether extract is concentrated 10:1.

With the apparatus assembled, regulate the furnace temperature at 260° ± 5° C. Cool the bubbling tube with ice while the end dips into petroleum ether. Regulate the nitrogen flow to ca. 200 ml. per min. Then introduce into the vertical glass "tank" 1 ml.

of petroleum ether vegetable extract corresponding to 10 g. of sample. Flow it into the system, then flow through the vertical tube 20 ml. of petroleum ether, at a constant rate, over a period of one hour.

Rinse the bubbling tube with petroleum ether; collect the washings in the receiving beaker. Concentrate this purified extract by transfer to a graduated conic tube and reduction of volume to 1 ml.

Inject into the chromatograph 2 µl. of this purified extract, a quantity equivalent to 20 mg. of the parent sample.

RESULTS

In this way we have purified extracts of different fruits and vegetables such as apples, beans, cabbages, carrots, green peas, oranges, potatoes, radishes, and tomatoes.

The electron capture gas chromatograms of these extracts show that the purification is satisfactory, with no "background" interferences for the organochlorine pesticides. However, samples of carrots have contained two or three unidentified substances as revealed by the electron capture detector; these compounds act like organochlorine insecticides upon chromatography through Florisil columns.

The method, when used precisely as described above, gives good separation between pesticides and the normally extracted interfering compounds. We have fortified crude fruit and vegetable extracts with from 0.02 to 0.12 p.p.m. of several pesticides, with good recoveries, as shown in Table I.

TABLE 1

Recovery of pesticides added to uncontaminated extracts of fruits and vegetables (apples, green peas, potatoes, radishes, and tomatoes)

Pesticide	Recovery (%)	Pesticide	Recovery (%)
BHC	100	<u>o</u>, <u>p</u>'-DDT	100
Lindane	100	<u>p</u>, <u>p</u>'-DDT	95-100
Heptachlor	100	Dieldrin	100
Heptachlor epoxide	100	Endrin	100
Aldrin	100	Chlordan	100
<u>o</u>, <u>p</u>'-DDE	100	Toxaphene	95
<u>p</u>, <u>p</u>'-DDE	100	Kelthane	100
		Methoxychlor	75

CONCLUSIONS

Selective partition by vapor solvent sweeping, on borosilicate wool, of organochlorine pesticides from fruit and vegetable extracts in the present apparatus and with the present technique provides sufficient cleanup for subsequent electron capture detector analysis. Amounts of organochlorine pesticides from 0.02 to 0.1 p.p.m. in fruits and vegetables are quantitatively recovered and can be analyzed by this method. This study, like those of GUNTHER <u>et al</u>. (2,3) with organochlorine pesticide residues in butterfat and in alfalfa and of STORHERR and WATTS (4) with organophosphate pesticides in several fruits and vegetables confirms that forced volatilization cleanup is a promising method.

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