Forced Volatilization Cleanup for Gas Chromatographic Assay of Pesticide Residues*

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A major deterrent to the widespread routine application of gas chromatographic segregative techniques and selective detectors to qualitative and quantitative pesticide and other residue evaluation has been "poisoning" of volatilization chamber and column by extraneous extractives. This present note is prompted by the recent publication by STORHERR and WATTS (1) of their "sweep codistillation" cleanup method, which is a version of our "forced volatilization" cleanup technique [OTT and GUNTHER (2)] as applied to butterfat. The final versions of our apparatus were best suited to cleanup of certain pesticides in butterfat, but the intermediate versions, described herein and in part by GUNTHER (3) were applicable with good recoveries to a variety of substrate extractives including the very intractable extractives mixture from alfalfa. All these devices physically separate gas chromatographable compounds from those compounds not

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gas chromatographable and provide a simple and versatile approach to the cleanup of stripping solutions to eliminate many extraneous extractives for almost any subsequent analytical operations.

Method and Apparatus

This cleanup procedure consists of hypodermically injecting a sample solution into a reproducibly heated chamber, sweeping the volatile materials through an aerosol filter and away from those that possess little or no volatility, then trapping the volatiles for further gas chromatographic or other scrutiny; the less volatile residuum is mechanically discarded from the apparatus. If desired, a section of gas chromatographic column packing can be placed in the apparatus to achieve any desired degree of retention of unwanted low-volatility compounds; appropriate choices of nature and of amount of column packing will often provide compounds sufficiently cleaned up for direct ultraviolet or infrared assay, for example. Also, the device can be adapted for either macro- or microscale separations.

In Figure 1 is shown one version of the basic design of this device.

Shown in more detail in Figure 2 is the volatilization portion of this simple device.

An even simpler version shown in Figure 3 accomplishes the same purpose. One advantage of this latter design is ease of removing the non-volatile residuum, which adheres to a replaceable wad of clean glass wool placed near the inlet end. The design of any volatilization cleanup device may be varied to suit supplies,

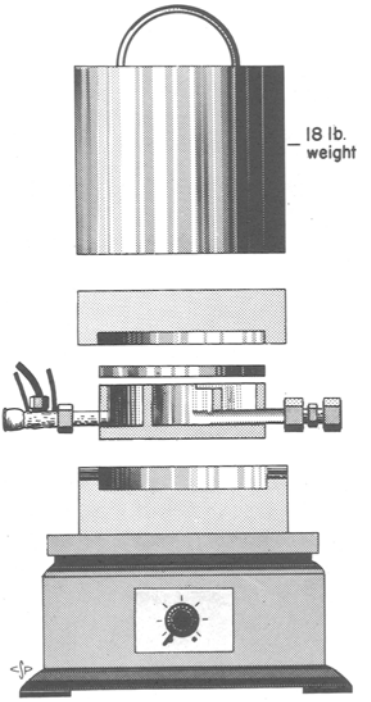

Fig. 1. Volatilization cleanup device constructed of aluminum. Component parts in ascending order are: thermostatically controlled hot plate, lower heat sink, volatilization chamber, lid for volatilization chamber, (lid sealed with a high-vacuum silicone lubricant), upper heat sink, and 18-lb. steel weight. Reproduced from GUNTHER (3) with permission

needs, and desires, but temperature profiles within the volatilization chambers must be reproducible.

In Figure 4 is shown the design of a special scrubber used for trapping the volatile eluants with the necessarily high rate of carrier gas flow, as discussed by OTT and GUNTHER (2). The

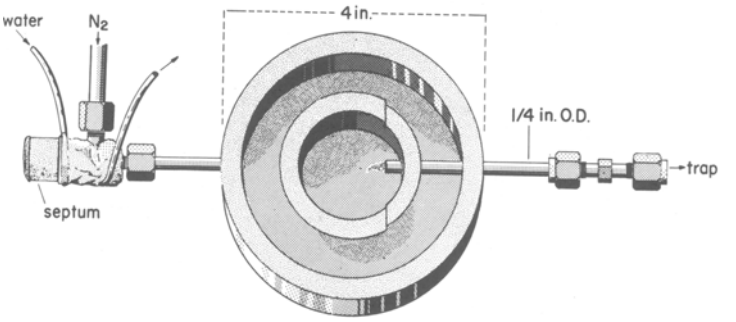

Fig. 2. Volatilization chamber of a cleanup device. The central chamber is usually filled with gas-chromatographic column packing on glass or quartz wool, and the outer section near the injection port is one-third filled with ignited sea sand. Reproduced from GUNTHER (3) with permission

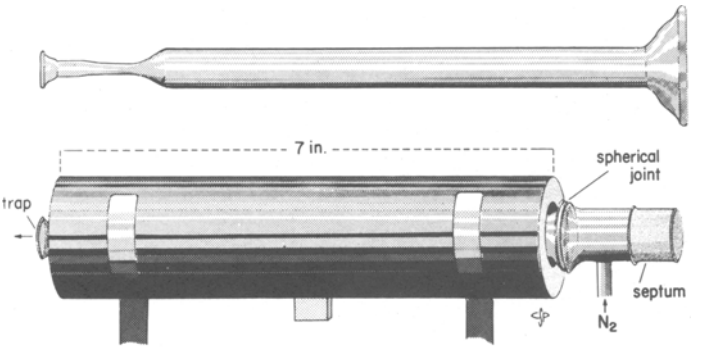

Fig. 3. Volatilization cleanup device constructed entirely of glass or quartz. Furnace is controlled by means of a variable resistor

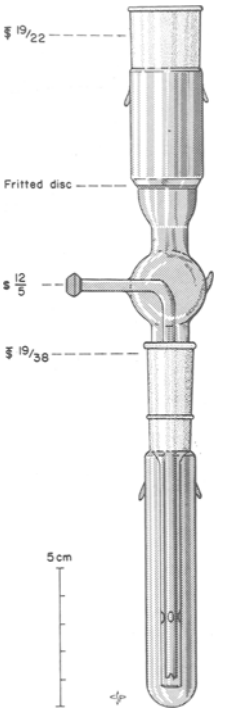

Fig. 4. Scrubber used for trapping volatiles in a high-flow gas stream (two-thirds actual size). The sintered glass disc is coarse porosity. The slot at the bubbler tip decreases bubble size. Emerging bubbles create a gas lift-pump, releasing slugs of solvent through the holes in the inner member and thus violently circulating the scrubbing solvent. At the end of a "run", the joint is loosened and the liquid in the "funnel" drains down the inner member to rinse it. Reproduced from GUNTHER (3) with permission

tube is the conventional Kuderna-Danish type [GUNTHER and BLINN (4)], and the solvent of choice is placed both in the tube and in the fritted glass scrubber to prevent entrainment losses.

Presented in Table I are the recoveries achieved with several

TABLE I

Percent recoveries[a/] of pesticides through volatilization cleanup devices

Pesticide	Construction material: GLASS — Glass wool Packing	GLASS — Glass wool & silicone-coated firebrick packing	ALUMINUM — Sea sand & silicone-coated firebrick packing
	(%)	(%)	(%)
Aldrin	94 ± 8	--	90 ± 7
Carbaryl[b/]	50,62	64,67	66 ± 2
DDT	77 ± 2	82,77	80 ± 2 DDT (38% as DDE)
DDE[c/]	103 ± 5	66,57	85 ± 5
p,p'-Dichlorobenzophenone[d/]	90,75	77	93 ± 4
Dieldrin	100 ± 5	--	90 ± 4
Ethion	69,68	--	69 ± 1
Kelthane[e/]	--	62,38	84 ± 3
Lindane[f/]	--	--	85 ± 4
Malathion	44 ± 8	--	69 ± 7
Parathion	46,36	62,77	69 ± 7
Tetradifon	71 ± 7	51,52	80 ± 3

a/ By infrared assay except as indicated.
b/ Appeared as α-naphthol.
c/ Product from p,p'-DDT.
d/ Product from p,p'-DDT and Kelthane.
e/ Appeared as p,p'-dichlorobenzophenone.
f/ Percent recovery by microcoulometric titration after combustion.

purified pesticides to demonstrate broad versatility under empirical but uniform developmental conditions. The temperature was 250° C., the nitrogen flow rate was 250 ml./minute, and the collection period

was 10 minutes.

Discussion

It must be emphasized that the above conditions were selected arbitrarily; optimum forced volatilization conditions for each compound of interest must be determined in advance of a residue study, then evaluated in the presence of the substrate extractives of interest. Work with actual stripping solutions, such as those involving DDT in alfalfa and in butter, indicates that with inefficient agitation or "turnover" of extractives from an insufficient gas stream flow rate recoveries are affected by the amounts and natures of non-volatiles introduced into the apparatus. Preliminary dewaxing, selective adsorption, or partitioning may sometimes still be desirable to reduce the bulk of these "keepers." Also, efficient thin-layer distribution on the glass wool or sand plus more efficient heat transfer for volatilization can be improved; fine inert metal granules sometimes improve heat-transfer. A vertical unit achieved improved "sweeping" abilities out of masses of oily extractives [e.g., butter as discussed by OTT and GUNTHER (2)] by permitting a high carrier gas flow rate without carry-over of excessive amounts of non-volatiles.

It is the main purpose of this report to reaffirm the great promise of this completely physical type of cleanup, not only for gas chromatography where volatilization chamber and column "poisoning" are major deterrents to really reliable widespread use, but also for almost any residue evaluation in which cleanup is a problem. It must be emphasized that some pesticides will

decompose thermally under these conditions (2,5,6 and cf. Table I) or may be attacked by the free alkali present even in (and on the surface of) borosilicate glass. Thus mg. quantities of p,p-DDT cycled several times through the glass version of Figure 3 were quantitatively dehydrochlorinated, and lindane yielded the usual mixed trichlorobenzenes; dehydrochlorination did not occur, however, when an all-quartz system was used.

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