

Determination of Organic Chlorides and Residues from Chlorinated Pesticides by Combustion Analysis

J. A. HUDY and C. L. DUNN
Research Center, Hercules Powder
Co., Wilmington, Del.

Analysis for traces of residues from chlorinated pesticides by combustion methods offers many advantages over other decomposition methods which involve chemical reagents. Available microcombustion procedures sometimes lack sensitivity because of a limitation on the size of sample which can be burned. Therefore, a vertical, quartz-packed furnace was developed, which features the ability to burn liquid organic materials continuously at rates of 10 to 20 grams per hour. The chloride resulting from combustion is determined by amperometric titration with silver nitrate after absorption in alkaline solution. A sensitivity of 5 γ of chloride has been achieved upon application of the method to toxaphene (chlorinated camphene, 67 to 69% chlorine) in a variety of materials, including animal fat and butterfat.

IN THE DETERMINATION of small amounts of residues from chlorinated pesticides in agricultural products, the problem arises of obtaining accurate results in the presence of large quantities of extraneous materials, which are extracted along with the pesticide. These materials include a variety of oils, fats, waxes, and other more or less saponifiable compounds.

Chemical means of reducing the halogenated pesticide to titratable form not only may introduce additional halides into the system, but also may hinder the effective use of highly sensitive titration techniques because of the large volume of solvent necessary to keep the resulting salts in solution.

These disadvantages have led in recent years to the use of combustion analysis as a tool for determining small quantities of chlorinated materials. In this type of analysis, the extraneous organic material is burned off and the halogen is collected in an aqueous absorber system. This technique not only yields a low "blank" value, but also allows the absorber solution to be evaporated and the halide to be further concentrated for the application of highly sensitive procedures such as amperometric titration (5, 6).

Microchemists often use such combustion methods (3) and similar techniques have been adapted to the analysis of chlorinated pesticide residues (1). The success of these adaptations has been possible through utilization of chromatographic and other separation techniques which concentrate the pesticide residue in a relatively small sample (<1 gram). For some types of samples, however, suitable separation methods are not always available. These include samples of fats and oils of vegetable and animal origin. In such cases, it is frequently

necessary to burn the sample directly, which immediately affects the utility of micro-type furnaces with limited sample capacity.

During the determination of toxaphene (chlorinated camphene, 67 to 69% chlorine) residues in agricultural materials, the authors have been confronted with analyses for which the conventional sodium reduction method (7) lacked suitable sensitivity. Some materials were not conveniently handled by the usual microanalytical combustion procedures because of sample-size limitation which seriously impaired sensitivity.

To overcome the sample-size limitation and still accomplish the desired

sensitivity, a vertical drip-type combustion furnace was used which was earlier developed in this laboratory for the determination of small amounts of sulfur in organic compounds (4). This apparatus featured the ability to burn large quantities of sample in a relatively short time. Its versatility and the ease with which samples covering a wide range of volatility could be burned made it appear readily adaptable to pesticide analysis.

Description of Apparatus

The combustion train is pictured diagrammatically in Figure 1. The dual

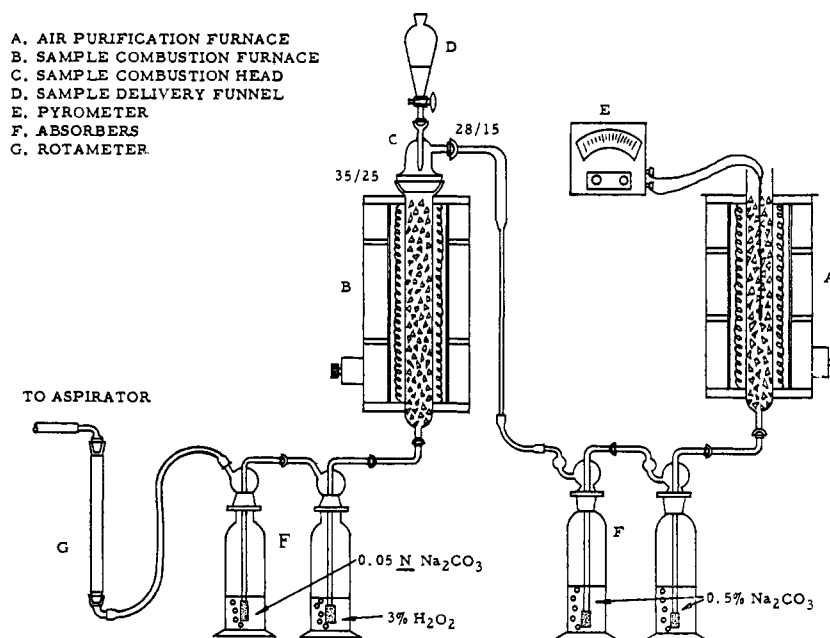


Figure 1. Combustion train

furnaces are operated in series, the first unit serving to purify the air for the second unit in which the sample is burned. The combustion tubes consist of 1.25-inch outside-diameter glazed quartz tube 14 inches in length. The lower end of each tube is constricted, and the inner member of a 12/5 spherical quartz joint is attached. An outer member of a 35/25 spherical quartz joint is attached to the top of the sample combustion tube to accommodate the combustion head and sample delivery apparatus. Each tube is packed with freshly ignited 6- to 8-mesh quartz chips and is heated by two Type 77 semicylindrical Nichrome heating units, commercially available from the Hevi Duty Electric Co., Milwaukee, Wis. These units are connected in parallel. Voltage input (0 to 70 volts) is controlled by means of separate Variacs of 15-ampere capacity. The temperature of the preburner furnace is measured continuously by a pyrometer and Chromel-Alumel thermocouple inserted in the core of the combustion tube. This same tube, with thermocouple, is used for periodic checks on the sample combustion furnace. The heater assembly is mounted in an aluminum shell by means of Transite disks. The shell is 5 inches in diameter and 12.5 inches long, and is packed with vermiculite insulation.

The sample combustion tube is supported at the lower end by an insulated ring and handle. The spherical joint connections, together with a flexible sliding mounting for the combustion head, allow approximately a 3-inch vertical movement of the combustion tube in the furnace.

The sample feed apparatus is limited to liquid samples and consists of a glass combustion head with detachable funnel or offset buret. The buret-type feed is used for volatile samples and the funnel-type feed is used for less volatile samples, such as fats, which may be melted prior to combustion and maintained in the molten state by the heat rising from the furnace.

Air to support combustion is drawn through the system at 7 to 9 liters per minute by means of an aspirator and is measured by a rotameter. The two absorber trains consist of 125-ml. standard tall-form gas-washing bottles fitted with extra coarse fritted-glass disks or rod-filled bubblers. The entire absorption train is placed in an ice bath to prevent excessive evaporation of absorbent.

Procedure

Combustion. The apparatus is assembled as in Figure 1. The temperature of the air purification furnace is brought to 950° to 1000° C. and the temperature of the sample combustion furnace is regulated simultaneously as follows:

For samples boiling below 200° C. the furnace temperature is adjusted to approximately 900° C.; for higher boiling samples (fats and heavy oils) the temperature is adjusted to approximately 950° C.

The absorbers are charged by adding 100 ml. of 0.5% sodium carbonate to each of the absorbers for the air purification train, 25 ml. of 3% hydrogen peroxide to the first sample absorber, and 25 ml. of 0.05*N* sodium carbonate to the second sample absorber. The absorbers are placed in an ice bath.

The sample is weighed or measured into the sample delivery apparatus. For low-boiling liquid samples the buret-type feed is recommended. For higher boiling materials and fats the funnel-type feed is more satisfactory. Fats or waxes are first melted before transfer to the delivery funnel, or these samples may be transferred to the delivery funnel and melted by suspending the funnel above a steam bath. Ordinarily, most fats can be burned directly and will stay molten in the heat radiated from the furnace. In some cases, the addition of a small amount of chloride-free solvent will help keep samples in liquid form.

A coating of silicone stopcock lubricant is applied to all joints. The combustion head and connecting tubes are attached to the furnace by means of spring clamps.

Air is drawn through the furnace at 8 liters per minute by means of an aspirator and all joints are checked to detect any bleeding of outside air into the system. The sample is introduced in a dropwise manner by careful adjustment of the sample delivery stopcock. Materials vary greatly in the rates at which they can be burned, but in general 1 drop every 3 seconds is satisfactory. The

position of the sample combustion tube in the furnace is adjusted to bring about gradual and complete volatilization of sample.

When the sample level has fallen to the delivery stopcock, the funnel or buret is rinsed with a small amount of chloride-free solvent, such as isopropyl alcohol, and the rinsings are burned. The last few drops of sample remaining in the delivery tip may be burned by allowing them to be carefully drawn in by the partial vacuum in the system.

The sample furnace temperature is then adjusted to approximately 1000° C. by means of the Variac. The combustion tube is lowered into the furnace as far as it will go, and the air-flow rate is maintained at 8 liters per minute for about 10 minutes. The air flow is then gradually reduced by 3-liter-per-minute increments at 5-minute intervals until an air flow of less than 1 liter per minute is reached. This rate is maintained until all carbonaceous residues present in the upper quartz volatilization area are burned off. The combustion tube is then raised in the furnace and the Variac returned to a setting which will prepare the furnace for the next combustion.

At the completion of this step, the air flow is turned off, and simultaneously the connection between the sample combustion furnace and absorbers is opened to prevent suck-back of the absorber solution.

Determination of Chlorinated Materials. Although designed specifically for the determination of microgram quantities of chlorinated materials, the apparatus is able to handle samples containing much higher concentrations of halogenated material. Table I shows results obtained on solutions containing

Table I. Analysis of Isopropyl Alcohol Solutions Containing Known Amounts of Halogenated Materials

Material	Chlorine, ^a Mg.	
	Added	Found
Chlorobenzene	0.95	1.06
	0.86	0.98
	0.79	0.83
	0.57	0.57, 0.55, 0.55
	0.46	0.47
	0.42	0.42
Epichlorohydrin	1.05	1.01
	0.86	0.82
	0.61	0.59
	0.58	0.58
	0.49	0.52
	0.36	0.36
	0.28	0.25
	0.16	0.17, 0.18
Toxaphene (chlorinated camphene, 67-69% Cl)	1.47	1.55
	1.38	1.35
	1.34	1.33, 1.35, 1.39, 1.43
	1.13	1.08, 1.14
	0.99	0.99
	0.94	0.95, 0.99

^a Absorber reagent blank of 0.03 mg. subtracted in each case.

as much as 1 to 2 mg. of chlorinated material.

Because sample size is practically no problem, oxygenated solvents may be used as diluents for concentrated samples and in many cases as solvents for solid samples. Proper choice of oxygenated solvents may not only aid materially in the combustion of difficult samples, but serve as a means for easier handling and combustion of extremely volatile materials.

Total chloride was determined by amperometric titration with 0.005*N* silver nitrate using the conventional rotating platinum electrode as described by Laitinen (5).

Determination of Chlorinated Pesticide Residues. As with most pesticide residue analyses, preparation and extraction of the sample is frequently the most time-consuming step. These phases of the analyses are beyond the scope of this paper. However, water-washing of the sample or sample extract is effective in removing inorganic halides from the sample prior to combustion. This step is particularly necessary in the case of animal fats, because they may contain considerable amounts of inorganic salts, which would deposit on the combustion tube packing and slowly leach out to contaminate future analyses.

As animal fats and butterfat may require highly sensitive analytical procedures because of the nature and size of the sample, work has been concentrated on the analysis of these types of samples. In most cases animal fats may be burned directly after rendering and washing. Various techniques are available for the extraction of butterfat (2), but in general the end product after evaporation of solvent is solid butterfat which may be melted and then burned directly.

As the quantities of material determined are usually in the trace category, considerable preliminary analyses and analyses of known samples are an essential part of the program. Possible contamination from the air, solvents, and other sources must also be investigated and reduced to a minimum.

In Table II are shown typical analyses of solutions containing microgram quantities of toxaphene (chlorinated camphene, 67 to 69% chlorine) to demonstrate the precision and accuracy which can be expected in analyses at the 1- to 50- γ level. In this series of determinations, the sample size varied from 2 to 10 grams. Recovery to within 3 to 5 γ of toxaphene is shown by these results. Total chloride was determined by amperometric titration with 0.005*N* silver nitrate using a rotating platinum micro-electrode (6).

In Table III are shown results of a series of analyses of butterfat samples which had been extracted from milk according to accepted procedures (2) and to which had been added small amounts

Table II. Analysis of Solutions Containing Known Amounts of Toxaphene

(Chlorinated camphene 67-69% Cl)

Material	Toxaphene, γ^a		Mean	S.D.
	Added	Found		
Terpene hydrocarbons	5	4, 4, 5, 3, 8, 3	5	2
	10	13, 4, 8	8	4
	20	17, 22, 29, 21	22	4
Animal fat	5	3	3	...
	10	13, 10, 13	12	1
	20	18	18	...
	30	23	23	...
	50	54	54	...
Butterfat	5	8, 6, 10	8	1
	7	10	10	...
	8	10	10	...
	10	13, 21, 16, 9, 14	15	4

^a Absorber reagent blank of 11 γ subtracted in each case.

of toxaphene. The concentrations of toxaphene shown should not be construed as typical values but demonstrate the range over which the present method of analysis was tested.

An average sensitivity of 3 γ of toxaphene is shown by the procedure in the 5- to 50- γ range. The advantage of unrestricted sample size is clearly shown by these results. As the amount of residue determined approaches the sensitivity of the method, accurate results are achieved by simply increasing the sample size accordingly.

Discussion

In the combustion of samples containing halogenated materials, the peroxide-carbonate absorber system was entirely satisfactory. At higher concentrations of chloride one may wish to increase the sodium carbonate concentration from 0.05*N* to 1 or 2*N*, but there is no need for reducing agents in conjunction with

halogen absorption in this apparatus. This hydrogen peroxide absorber is included to oxidize further sulfur-containing compounds which might be titrated in the final amperometric titration. As this solution would readily decompose under alkaline conditions, it is placed in a separate absorber.

Samples vary considerably in their volatility, but in general, approximately 6 minutes is required to burn a 1-gram sample of fat, not including the 0.5-hour afterburning period which is used to ensure complete removal of halogens and carbonaceous residues from the combustion tube. Liquid samples up to 20 grams can conveniently be burned by the described apparatus, although the only limit on sample size is the time allotted for combustion. Samples more volatile than fats may be burned more rapidly, and combustion rates of 15 to 30 grams per hour may be obtained with samples of alcohol or some hydrocarbon extracts. Benzene is difficult to burn smoothly, and it has been the practice to evaporate

Table III. Analysis of Butterfat Containing Known Amounts of Toxaphene

(Chlorinated camphene 67-69% Cl)

Sample Burned, Grams	Toxaphene, γ^a		Toxaphene, P.P.M.	
	Added	Found	Added	Found
2.7	50	56	18.5	20.7
5.2	50	53	9.6	10.2
5.0	50	51	10.0	10.2
2.7	20	23	7.4	8.5
	20	21	7.4	7.8
	10	14	3.7	5.2
	10	9	3.7	3.3
5.5	10	9	1.8	1.6
	10	9	1.8	1.6
10.7	10	8	0.90	0.80
	10	15	0.90	1.40
5.5	5	6	0.91	1.10
10.6	5	3	0.47	0.28
10.5	5	11	0.48	1.00
10.3	5	9	0.49	0.87
10.2	5	8	0.49	0.78
19.7	5	9	0.25	0.45
19.8	5	5	0.25	0.25

^a Absorber reagent blank of 11 γ subtracted in each case.

this solvent and replace it with one of the alcohols.

The apparatus is versatile in handling materials of varying volatilities. By raising or lowering the combustion tube in the furnace and adjusting the furnace temperature, materials ranging from vegetable oils to low-boiling alcohols or ethers may be burned. In the case of extremely volatile materials, the offset buret feed may be employed. Small samples may also be diluted with other solvents to obtain a mixture of medium volatility.

No explosions have occurred with the combustion apparatus, even when highly volatile materials such as ether-isopropyl alcohol mixtures were handled. The large air-to-sample ratio probably serves to prevent the formation of explosive mixtures.

Samples must be free from undissolved particles which impede sample flow. In the case of inorganic impurities, such as

boiling chips, a filtration is sufficient, but difficultly soluble organic materials may require heating or other solvents to bring about smooth sample flow.

Silicone stopcock lubricant was found to be of considerable value in sealing the spherical joints in the apparatus, particularly those affected by the heat of the furnace. The spherical joints should be cleaned occasionally to prevent a build-up of granular deposits which may allow outside air to bleed into the system.

A piece of Tygon tubing provides flexibility between the air purification train and combustion furnace assembly. However, this material should not be used for connections between absorbers or in connections which are subject to heat because of the danger of contamination.

The described apparatus has been in use for residue analyses in this laboratory for several years. It offers advantages over available equipment in regard to

simplicity and utility, especially where sample size is a limitation on sensitivity.

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ZINC DETERMINATION

Determination of Zinc in Plants and Soils

E. T. VERDIER, W. J. A. STEYN,
and D. J. EVE

Rhodes University, Grahamstown,
South Africa

A critical investigation of the reliability of the dithizone and polarographic methods, for the determination of zinc, is presented. A satisfactory modification of the Cowling and Miller dithizone photometric method was devised by the close study of the influence of pH on zinc extraction, transmittance curves, and accuracy of the technique. With this modified procedure, 24 zinc determinations per day could be carried out. A modified polarographic method, aimed especially at the elimination of a preliminary separation step was found to lend itself also to the simultaneous determination of copper, nickel, manganese, and possibly cobalt.

Study of Dithizone Photometric Method

ZINC IN BIOLOGICAL MATERIALS has been determined most commonly by either photometric procedures, based on the red complex which zinc forms with diphenylthiocarbazone, usually referred to as "dithizone," or polarographic methods. Both of these methods were selected for careful study.

The most popular dithizone method is that of Cowling and Miller (2), published in 1941. Since then many workers have presented modifications of this method (5-7, 14-17). The majority

of these were aimed at a reduction in the time of the lengthy extraction technique employed by Cowling and Miller. However, in many cases, a loss of accuracy was involved by the modification.

The essential feature of the Cowling and Miller method consisted in a three-stage extraction technique. First, the zinc and other metals forming dithizone complexes were separated from iron, aluminum, calcium, and other substances by extracting the sample solution, buffered at a pH of 8.5, with a dithizone-

carbon tetrachloride solution. The zinc was next separated from copper by extracting the organic phase with a dilute hydrochloric acid solution. Finally, the acid solution was neutralized, buffered at pH 8.5 with ammonium citrate-ammonia solution containing some sodium diethyl dithiocarbamate, and the zinc extracted with dithizone as before. Photometric measurements were carried out on a portion of the zinc dithizonate extract at a wave length of 530 to 540 $m\mu$ (17).

The critical points in this method which were selected for closer study were the effect of pH on the quantitative