

## Determination of Total Chlorine in Pesticides by Reduction with a Liquid Anhydrous Ammonia-Sodium Mixture

HERMAN F. BECKMAN, EDWARD R. IBERT, B. B. ADAMS, and D. O. SKOVLIN<sup>1</sup>

State Chemist Laboratory, Texas Agricultural Experiment Station, College Station, Tex.

Sodium reduction in anhydrous ammonia has been applied to the determination of total halides in insecticides. The method is fast and requires very little sample handling. Samples may be completely analyzed in 30 minutes. The method should be of particular interest to pesticide manufacturers and regulatory agencies. With slight adaptation, the technique could be applied to residue studies.

CHLORINATED PESTICIDES, or products containing these materials, may sometimes be adequately analyzed by chromatographic separations or specific color tests. When these methods cannot be applied, the total amount of organically bound chlorine must be determined. This nonspecific procedure is acceptable because there are so few naturally occurring organic halides.

The two methods most widely used for determining organic chlorides are the sodium-alcohol reduction and combustion techniques (7-6, 11, 13). Phillips and De Benedictis (12) found the sodium-alcohol method unsatisfactory for certain pesticides, unless isobutyl alcohol replaced isopropyl alcohol. In some other cases, with no explainable cause, the sodium-alcohol procedure fails to dechlorinate pesticides. The combustion technique, while giving excellent results, is difficult to employ as a routine procedure because of the length of time and manipulations necessary. Organic chlorine procedures containing modifications in titration, sample handling, and processes of breaking the chlorine away from the organic part of the molecule are well known. Some pesticides contain halogens which are considered labile; the halide may be stripped off with an aqueous or alcoholic solution of an alkali. An early paper describes this process for determining labile halide (15). The present paper proposes determination of chlorinated pesticides by a reduction technique which has not been used for this purpose.

Gould (10) noted that all the alkali metals are soluble in ammonia. They form a blue color in such solutions and are extremely good reducing agents. Use of liquid anhydrous ammonia (hereinafter termed ammonia) and sodium to dechlorinate organic compounds was reported by Chablay in 1914 (7). Clifford in 1919 (8), Vaughn and Nieuwland in 1931 (14), and Dains and Brewster in 1920 (9) used ammonia and sodium for the reducing medium on an

organic compound containing a halogen. Some of these authors were interested in the formation of cyanides by this process. Vaughn and Nieuwland found that acidification of the solution destroyed the effects of the cyanide in the titration of the halides. This reaction has been studied with the idea of applying it to pesticides.

The process has several advantages. The reaction takes place rapidly (1 to 2 minutes) compared to the hours of reflux and other manipulations required for the alcohol method. A minimum of equipment is needed; the reaction takes place in the beaker in which the titration is made. No chlorinated compound used as a pesticide has been encountered that will not give quantitative yields (see tables). Small quantities of sodium (0.5 gram or less) and of other reagents are required.

The procedure consists of two steps after the sample is weighed: solution in ammonia followed by sodium reduction, and neutralization and titration. Total elapsed time per sample on a series of samples can be as little as 30 minutes.

### Apparatus and Equipment

Anhydrous ammonia tank equipped with pressure gage (400-pound), bleed valve and safety valve, fill and take-off

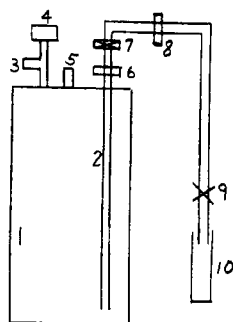


Figure 1. Schematic diagram of ammonia tank and valve assemblies

1. Ammonia tank. 2. Dip tube. 3. Pop-off valve. 4. Pressure gage. 5. Safety valve. 6, 8. Hoke valve, Type 303, S.S., Cat. No. 343. 7. Coupling. 9. Hoke valve, Type 303, S.S., Cat. No. 323. 10. Test tube

valve, and dip tube that runs nearly to bottom of tank.

Any dealer in agricultural anhydrous ammonia should be able to supply and install these properly, and fill the tank with ammonia. The tank can be of any size, but a 15-gallon tank has been found most satisfactory. When full of ammonia, it weighs but 140 pounds. A withdrawal assembly is attached to the filler valve through a coupling. Liquid can thus be drawn directly from the tank. Figure 1 shows the relative position of the valves and accessories on the tank.

A Fisher Titrimeter and a Sargent Ampot have been successfully used in the titration assembly.

### Reagents

Ammonia  
Ethyl ether  
Sodium, freshly cut into 1/8-inch cubes, stored in xylene  
Nitric acid, both concentrated and 1 to 1 with water  
Phenolphthalein, 1% in ethyl alcohol  
Standard solutions of silver nitrate and sodium chloride, 0.05N  
Hydrogen peroxide, 30%

### Procedure

Sufficient sample is weighed to yield 1 meq. of chlorine, transferred into a 400-ml. beaker, and covered with a watch glass. Ethyl ether (20 ml.) may be added to ensure solution in the ammonia. It is convenient to draw the ammonia into 25 × 250 mm. borosilicate glass test tubes. To chill the contents in order to prevent splattering, the beaker is placed in a Petri dish and about 20 ml. of ammonia are poured into the dish around the beaker. Then about 40 ml. of ammonia are added to the beaker and the watch glass is replaced. Two or three sodium cubes are added to the beaker and the beaker is swirled to stir the contents. When the whole mixture turns blue (about 1 to 2 minutes), the reaction is complete. After the permanent blue is obtained, the beaker is placed at the rear of the hood until

<sup>1</sup> Present address, Department of Chemistry, State University of Iowa, Iowa City, Iowa.

evaporation of the ammonia and ether is complete. Small amounts of moisture naturally condense into the cold mixture, which destroy the blue color and the sodium.

After the evaporation is complete, 30 ml. of distilled water are added to dissolve the residue. A drop of phenolphthalein is added and nitric acid and water (1 to 1) are added to the neutralization point. Then 10 ml. of concentrated nitric acid and 70 ml. of distilled water are added. The solution is then ready for titration.

If sulfur is present in the sample, its effects may be removed in a manner similar to that used in the sodium-alcohol procedure. After ammonia evaporation and addition of water (about 20 ml.), 10 ml. of 30% hydrogen peroxide are added and the beaker is placed on a hot plate. The contents are boiled gently for 10 minutes, and then neutralized as described above.

### Results and Discussion

One milliequivalent of chlorine has proved the most convenient sample size for pesticide formulations. For samples containing lesser amounts of chlorine, more dilute titrating solutions are employed. If residue studies are undertaken, procedures and precautions that normally attend such work should be imposed. This method can be adapted for such use and the analysis time materially shortened.

The hazard and difficulty in handling anhydrous ammonia as a liquid do not make the procedure in any way impractical. The ammonia was allowed to escape in a steady hissing stream through a needle valve set a few inches from the dripping tip. The expansion of the first few milliliters of the escaping gas lowers the temperature sufficiently to cause the following portions to liquefy. It can then be handled like any volatile solvent under a good standard hood. One necessary precaution is to handle all glassware with tongs. The temperature of liquid ammonia in equilibrium with its vapors at 1 atm. is  $-33^{\circ}\text{C}$ .

The results in Table I show that the method recovers essentially all the chlorine present in a sample. The percentage purities of the compounds given are those stated on the sample as received from the manufacturer. Calculations of recovery were based on this value. Toxaphene and chlordan, which are not pure compounds, were calculated to the chlorine guarantee.

Table II compares the results obtained by the two methods and the guarantee of the formulator of the commercial product. In each case the values for the ammonia procedure are slightly higher than by the sodium-isopropyl alcohol method. Thus the method proposed gives consistently better results. Several

samples failed to meet the guarantee of the formulator by the sodium-isopropyl alcohol method. When analyzed by the ammonia method, results were improved, in some cases. Samples that appeared to be giving trouble were chosen for comparisons.

In Table III, results by the sodium-ammonia method are compared with the

national average of some collaborative samples sent out by the Association of American Pesticide Control Officials. All collaborative data were obtained by the sodium-alcohol method. All samples were dusts, the heptachlor being in a mixed fertilizer. The sodium-alcohol method was chosen for making comparisons, as it was used routinely in this laboratory.

**Table I. Recovery of Chlorine from Pure Samples of Insecticides**

Compound	Purity, %	Recovery, % <sup>a</sup>
Dieldrin	99.6 <sup>b</sup>	99.6
Aldrin	99.3 <sup>c</sup>	100.7
Heptachlor	99.1 <sup>d</sup>	99.8
Lindane	100.0 <sup>e</sup>	101.1
BHC	99.0 $\pm$ 1.0 <sup>f</sup>	98.1
DDT	100.0 <sup>g</sup>	99.3
Toxaphene	(67.9% Cl) <sup>h</sup>	99.8
Chlordan	Purif. tech. <sup>i</sup>	101.5

<sup>a</sup> Calculations based on chlorine content expected from purity guarantee of manufacturer.

<sup>b</sup> 1,2,3,4,10,10 - Hexachloro - 6,7 - epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene.

<sup>c</sup> 1,2,3,4,10,10 - Hexachloro - 1,4,4a,5,8,8a - hexahydro - 1,4 - endo - exo - 5,8-dimethanonaphthalene.

<sup>d</sup> 3a,4,5,6,7,8,8 - Heptachloro - 3a,4,7,7a-tetrahydro-4,7-methanoindene.

<sup>e</sup> 99% gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane.

<sup>f</sup> Mixture of isomers of 1,2,3,4,5,6-hexachlorocyclohexane.

<sup>g</sup> 1,1,1 - Trichloro - 2,2 - bis(*p* - chlorophenyl)ethane.

<sup>h</sup> Defined as a mixture of chlorinated terpenes containing 67 to 69% chlorine.

<sup>i</sup> 1,2,4,5,6,7,8,8 - Octachloro - 2,3,3a,4,7,7a - hexahydro - 4,7 - methanoindene and related compounds.

**Table III. Comparison of Results**

Compound	Chlorine, %	
	National average	Found, Na-NH <sub>3</sub> method
DDT	47.96	47.88
Dieldrin	10.47	10.71
Heptachlor	0.51	0.49
Chlordan	39.07	38.97

### Literature Cited

- (1) Agazzi, E. J., Parks, T. D., Le Ferbe, H. A., Lykken, L., *Anal. Chem.* **24**, 1688 (1952).
- (2) Agazzi, E. J., Peters, E. D., Brooks, F. R., *Ibid.*, **25**, 237 (1953).
- (3) Assoc. Offic. Agr. Chemists, "Methods of Analysis," 8th ed., p. 408 1955.
- (4) Beamish, F. E., *Ind. Eng. Chem. Anal. Ed.* **5**, 348 (1933).
- (5) Carter, R. H., *Anal. Chem.* **19**, 54 (1947).
- (6) Carter, R. H., Hubanks, P. E., *J. Assoc. Offic. Agr. Chemists* **29**, 112 (1946).
- (7) Chablay, E., *Ann. chim. phys.* **1** (9), 469-519 (1914).
- (8) Clifford, C. W., *J. Am. Chem. Soc.* **41**, 1051-60 (1919).
- (9) Dains, F. B., Brewster, R. Z., *Ibid.*, **42**, 1573-9 (1920).
- (10) Gould, E. S., "Inorganic Reactions and Structure," p. 101, Henry Holt, New York, 1955.
- (11) Parr, S. W., *J. Am. Chem. Soc.* **30**, 764-70 (1908).
- (12) Phillips, W. F., De Benedictis, M. E., *J. Agr. Food Chem.* **2**, 1226-8 (1954).
- (13) Pringsheim, H. S., *Am. Chem. J.* **41**, 386 (1904).
- (14) Vaughn, T. H., Nieuwland, J. A., *Ind. Eng. Chem., Anal. Ed.* **3**, 274-5 (1931).
- (15) Winter, P. K., *Ibid.*, **15**, 571-4 (1943).

Received for review December 26, 1956. Accepted August 21, 1957. Division of Agricultural and Food Chemistry, 131st Meeting, ACS, Miami, Fla., 1957. Work done under Research Project 1111, Texas Agricultural Experiment Station.

**Table II. Comparison of Results**

Compound	Chlorine, %		
	Guarantee	Method	
		Ammonia	Sodium-isopropyl alcohol
BHC	33.6	32.1	31.7
DDT	25.0	25.7	
	25.0	28.1	
DDT-BHC	14.6 Cl	15.7	15.3
DDT-toxaphene	36.8 Cl	36.4	35.6
	36.8 Cl	36.6	
Toxaphene	60.0	54.4	54.1
Aldrin	23.0	25.6	25.6
Chlordan	10.0	9.0	8.3
	10.0	9.0	
Dieldrin	18.7	19.7	
	18.6	18.2	
	18.6	18.7	
Endrin	19.8	22.9	
Heptachlor	31.0	29.8	