

Determination of Trace Amounts of Lindane in Air by Infrared Spectrophotometry

P. E. BRAID and JOSEPH LeBOEUF

Occupational Health Division, Department of National Health and Welfare, Ottawa, Canada

► Low concentrations of lindane in air, such as are encountered in environmental health studies, can be detected by the method described. Three persistent infrared absorption peaks at 845, 698, and 685 cm^{-1} characterize this insecticide, the 685- cm^{-1} peak being used for quantitative determination. With air samples of 50 cubic feet collected by adsorption on granular alumina at a flow rate of 1 cubic foot per minute, concentrations of lindane in air from 1 to 100 γ per cubic foot may be measured. The lindane is removed from the adsorbent by means of hot iso-octane, which is then evaporated to a small volume and transferred to an infrared cell for measurement.

LINDANE, the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane of at least 99% purity, has found widespread use in recent years. It is frequently necessary to determine concentrations of the vapor of suspended particles in air, either in connection with entomological studies or for comparison of measured levels with established tolerance limits for human exposure.

Colorimetric methods for the estimation of small amounts of lindane have been described (6, 8) and one has been employed in the determination of lindane residues in air (4). However, such methods, although usually adequate for entomological studies, are not specific for lindane and are subject to certain interferences. For determinations of lindane in environmental health studies, the far greater specificity of infrared spectrophotometry is preferred. While the procedure described here requires a minimum sample of 50 γ of lindane as against 5 or 10 γ for colorimetric procedures, the disadvantage of this lower sensitivity has been minimized by increasing the rate of air sampling.

EXPERIMENTAL

The air sampling apparatus consists of an absorption tube (Figure 1) of 2.5-cm. diameter containing a column of alumina 2.5 cm. long held between glass wool plugs. The absorbing action in the tube consists of entrainment of

airborne particles of lindane mainly by the glass wool plug at the inlet end of the tube and adsorption of the vapor by the granular adsorbent (80- to 200-mesh absorption alumina, Fisher Scientific Co.). For field tests the tube was mounted in a vertical position in the test atmosphere with the upper part (24/40 inner member reduced to 8-mm. tube size) removed.

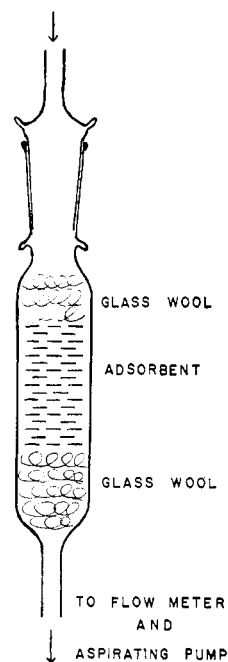


Figure 1. Absorber for collection of lindane in air

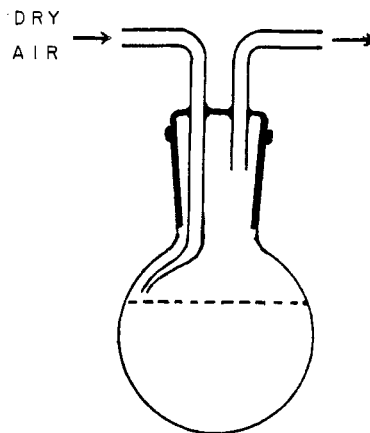


Figure 2. Evaporator for reduction of extractant to small volume

Air was aspirated through the tube in series with a dry gas meter by means of an electrically driven air pump with a capacity of about 1.3 cubic feet per minute. In order to keep sampling time as short as possible, high rates of flow were tried. With two absorbing tubes in series and a flow rate of 1 cubic foot per minute, under all normal conditions of temperature and humidity no detectable amount of lindane was carried over into the second absorber for the range of concentrations discussed here. Consequently, this sampling rate was adopted, the sample volume being 50 cubic feet for concentrations in the range from 1 to 100 γ of lindane per cubic foot of air. The total weight of lindane represented by these limits is 50 to 5000 γ . As this is dissolved in 0.5 ml. of solvent, the corresponding solution concentrations are 0.01 to 1.0 wt. per volume %.

The extraction of the lindane from the alumina was accomplished by pouring hot iso-octane (initially at 90° C.) through the inverted absorption tube in four 25-ml. aliquots and collecting the extract in a 125-ml. boiling flask. The iso-octane was certified material supplied by the Enjay Co., Inc. As the glass wool plug exposed to the incoming air during sampling collects practically all of the particulate lindane, it must be left in place during the extraction procedure. The boiling flask was fitted with a stopper equipped with two glass tubes to form an evaporator, as illustrated in Figure 2. Evaporation was accomplished by aspirating dry air through the flask while the temperature was kept at about 35° C. Evaporation to dryness, with consequent substantial loss of lindane, was avoided; a final sample volume of somewhat less than 0.5 ml. resulted in negligible loss of lindane.

The concentrated extract in the evaporator was adjusted to a volume of 0.5 ml. by drawing the solution up into a 1-ml. graduated hypodermic syringe fitted with a square-cut needle and adding iso-octane until the correct volume was obtained. The determination was performed on a Perkin-Elmer Model 21 double-beam spectrophotometer, with a cell of 1 mm. thickness containing the sample and compensated by a similar cell containing pure iso-octane which had been similarly evaporated to small volume.

The spectrum was scanned between the limits of 600 and 900 cm^{-1} (11.1 and 16.7 microns). Of the three peaks used to establish the presence of lindane (845, 698, and 685 cm^{-1} ; 11.8, 14.3,

and 14.6 microns) the persistent peak at 685 cm^{-1} was used for quantitative analyses.

The standard curves shown in Figure 3 were prepared from values for solutions of high purity lindane in iso-octane. In the analysis of unknown solutions the "standard method" curve was used in conjunction with the conventional base-line technique for measuring absorbance (3). For samples containing about 0.05% or less of lindane, the differential method of analysis (7) was used. This involves obtaining a tracing with sample in the sample beam and pure solvent in the reference beam and then repeating the procedure after interchanging sample solution and solvent. The standard curve for this method is based on peak-to-peak distances between the two bands lying on opposite sides of the base line.

By means of the generator shown in Figure 4, known and variable concentrations of lindane in air could be obtained to check and calibrate the collection and analysis procedure. Measured quantities of lindane were vaporized by means of a heater into a bell jar in which an upward-flowing air stream carried it along to the absorbing tube. The heating device was an indented, 60-watt light bulb of the type found in household thermal vaporizers for lindane. The heater temperature was controlled by means of a Variac.

Stock solutions of lindane in ether in concentrations of 0.01, 0.1, and 1.0% were placed in the depression in the bulb in amounts varying from 0.5 to 2.0 ml. The ether evaporated quickly with negligible loss of lindane. The deposit of lindane could then be evaporated into the air stream at any rate desired by controlling the bulb temperature. The bell jar was mounted on three 1/4-inch blocks so that the incoming air entered peripherally at the bottom. By adjusting bulb heat, total amount of lindane, and rate of air flow, high or low concentrations of lindane in air could be obtained, the total amount of lindane vaporized always being known. The dry gas meter (Sprague Zephyr, Model 1A), in the collecting system indicated the air flow rate and provided a record of total air volume.

DISCUSSION

The Canadian Standards Association specifies a rate of emission of lindane in occupied rooms not to exceed 0.000066 gram per 24 hours per cubic foot of treated space having 36 or more air changes per 24 hours (1). This amounts to a calculated maximum air concentration of 1.83 γ of lindane per cubic foot of air. The present technique requires a minimum sample of 50 γ of lindane; therefore, a 50-cubic foot sample taken at the rate of 1 cubic foot per minute was adopted. For air concentrations below 1 or above 100 γ per cubic foot, the air sample must be increased or decreased accordingly.

Iso-octane was used in the analytical procedure because the hot solvent is a

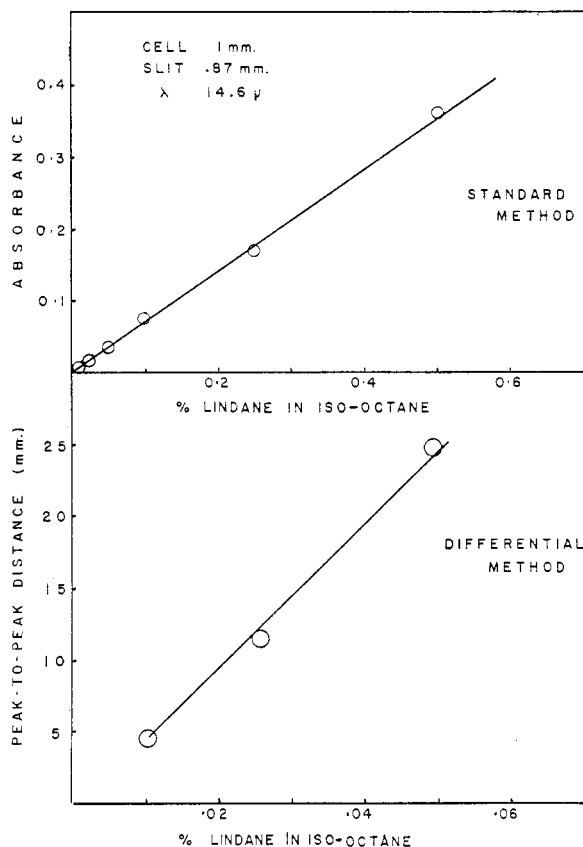


Figure 3. Standard curves for lindane in iso-octane solution

satisfactory extractant for lindane adsorbed on alumina and because it is one of the few satisfactory infrared solvents in 1-mm. cells in the region from 600 to 900 cm^{-1} . The transmittance is about 90% at 685 and 698 cm^{-1} and about 50% at 845 cm^{-1} . A solvent is generally considered acceptable at a given wave length if it transmits 25% or more of the incident energy (5).

The use of one solvent for extraction and analysis afforded a great simplification in the procedure. The somewhat low solubility of lindane in iso-octane (2% at 20°C.) was not of importance because no solutions exceeded 1% in concentration. Acetonitrile, which was tried as an alternate to iso-octane, is an acceptable infrared solvent in a 1-mm. cell in the 600 to 900 cm^{-1} region and is a good extractant for lindane adsorbed on alumina. It is also more volatile than iso-octane and therefore more readily evaporated to small volume. However, it had the disadvantage of partially decomposing to produce interfering substances during evaporation; it is also more toxic and more expensive than iso-octane.

The only three lindane bands of any importance in the rock salt region occur within the interval from 600 to 900 cm^{-1} . In most cases it is sufficient to scan this portion of the spectrum to establish the presence or absence of lindane, although occasionally it may be desirable to scan a greater region. The most sensitive

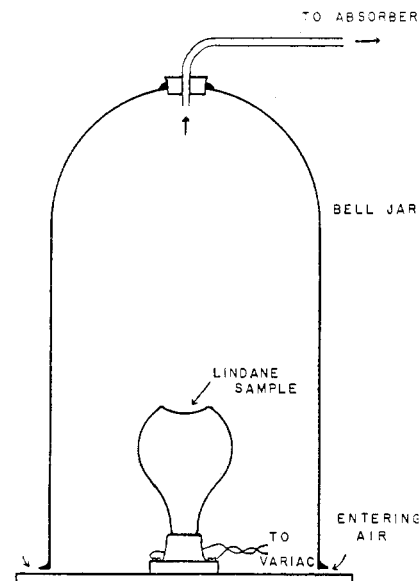


Figure 4. Apparatus for sublimation of lindane at controlled rates

685- cm^{-1} band has been used previously in quantitative analysis of the gamma isomer (2).

In the quantitative determination of lindane by the base-line technique, for solution concentration below about 0.05% the absorption is low and slight variation in the location of the base line may have a relatively large influence on the calculated concentration of lindane. For this reason the differential

Table I. Recovery of Lindane from Air Samples

Lindane Vaporized, γ	Total Air Flow through System, Cubic Feet	Equiv. Air Concn. of Lindane, γ per Cubic Foot	Percentage Recovery of Lindane
250	250	1	83
500	50	10	80
500	10	50	82
1000	10	100	78

method (7) is preferable for solution concentrations of 0.05% and under.

For measured quantities of lindane in a solvent introduced into the adsorbent bed, recovery was 100% when the extraction and analysis procedures described herein were applied. However, for lindane introduced into the adsorbent bed as a low concentration constituent of an air stream, recovery was approximately 80%, as shown in Table I. This recovery was simply allowed for in the present case. Recovery might be improved by heating the adsorbent just prior to extraction and/or increasing the volume of iso-octane extractant, but the subsequent evaporation of a large volume of extractant becomes tedious. The estimated accuracy of the method is $+3\%$ or $\pm 0.3 \gamma$ per liter of air, whichever is greater. Thus, at the extreme lower limit of range of the method, the accuracy is reduced to approximately $+30\%$.

The method described here was applied in atmospheres of not more than about 65% humidity. Although the effect was not investigated, it is possible that higher humidities would have an

adverse effect on the collection efficiency of the adsorbent.

RESULTS

The use of the method to assess both low and high concentrations of lindane in air is illustrated by two examples.

Lindane was vaporized at 0.50 gram per 24 hours into a 10,000-cubic foot room ventilated at an estimated 1.5 air changes per hour. The air concentration of lindane under these circumstances, assuming uniform dispersal and no absorption by surfaces, would be approximately 1.4γ per cubic foot. However, the actual value would be lower than this as a result of absorption of lindane by surfaces. The estimated actual value, based on experimental data of Tatro (9), would be approximately 0.36γ per cubic foot. This difference between the concentration emitted into the air and the measured air concentration is attributed partly to adsorption by surfaces but mainly to continuous absorption by wood and other structural materials. The value obtained by the method described

here, based on a 150-cubic foot air sample, was 0.35γ per cubic foot.

A 0.3-gram sample of lindane was vaporized into a 50-cubic foot fume hood to produce an initial air concentration of 6000γ of lindane per cubic foot as fume and saturated vapor. After 3 hours, at which time the concentration of lindane would be between 200 and 600γ per cubic foot as a result of particle settling, a 16-cubic foot sample was withdrawn and analyzed. The measured value (corrected for dilution by the sampling procedure) was 370γ per cubic foot.

LITERATURE CITED

- (1) Canadian Standards Association, Ottawa, Canada, C.S.A. Standard Z129-1954, Standard for Insecticide Vaporizers—Continuous Type (May 1954).
- (2) Daasch, L. W., *ANAL. CHEM.* **19**, 779-85 (1947).
- (3) Heigl, J. J., Bell, M. F., White, J. V., *Ibid.*, **19**, 293-8 (1947).
- (4) Hornstein, I., Sullivan, W. N., *Ibid.*, **25**, 496-8 (1953).
- (5) Jones, R. N., Lauzon, R., National Research Council, Ottawa, Canada, *NRC Bull.* **3** (1953).
- (6) Phillips, W. F., *ANAL. CHEM.* **24**, 1976-9 (1952).
- (7) Robinson, D. Z., *Ibid.*, **24**, 619-22 (1952).
- (8) Schechter, M. S., Hornstein, I., *Ibid.*, **24**, 544-8 (1952).
- (9) Tatro, M. C., Ph.D. thesis, University of Massachusetts, Amherst, Mass., 1952.

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Spectrophotometric Determination of Lithium Carbide in Metallic Lithium as the Acetylene—Silver Perchlorate Complex

T. W. GILBERT, Jr., A. S. MEYER, Jr., and J. C. WHITE

Oak Ridge National Laboratory, Oak Ridge, Tenn.

► Lithium carbide and lithium nitride in lithium metal are determined simultaneously by measuring the quantities of acetylene and ammonia that are evolved when a sample of lithium is dissolved in water. Ammonia is absorbed in a solution of boric acid and is determined by the conventional Nessler's method. Available methods for the determination of small amounts of acetylene either lacked the required sensitivity or were not suited to this application. Accordingly, a new spectrophotometric method was devised for the determination of 50 to

2500 γ of acetylene with a coefficient of variation of 2.7%. The acetylene is absorbed in 1.5M silver perchlorate; the ultraviolet absorption of the soluble silver-acetylene complex that is formed is then utilized for the determination of acetylene.

LITHIUM METAL is ordinarily contaminated by oxygen, nitrogen, and carbon which exist in the combined forms of lithium oxide, Li_2O , lithium nitride, Li_3N , and lithium carbide, Li_2C_2 , respectively. When the metal is dissolved in water, the nitride is

hydrolyzed quantitatively to ammonia and the carbide to acetylene. As hydrogen is also a product of the dissolution of metallic lithium in water, methods for the determination of carbon in lithium involve the determination of traces of acetylene in hydrogen. The purpose of this investigation was to develop a simple and rapid method for the determination of acetylene in hydrogen that would also allow simultaneous determination of the ammonia released by the hydrolysis of lithium nitride.

Small amounts of acetylene are gen-