

better than this, because this value was calculated without considering the variation in the samples themselves—i.e., milk samples collected from different animals on the same day were assumed to be identical.

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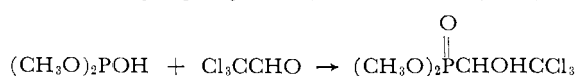
## INSECTICIDE ANALYSIS

# Polarographic Determination of *O,O*-Dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate (Bayer L 13/59)

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A polarographic procedure has been developed for the analysis of technical grades and formulations of *O,O*-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate, currently known as Bayer L 13/59. The reduction is carried out at  $25^{\circ} \pm 0.5^{\circ}$  C. in an aqueous solution containing 0.02*N* potassium chloride as the supporting electrolyte and 0.002% gelatin as the maximum suppressor. An accuracy of 2% is obtained under the specified conditions, and the half-wave potential against the saturated calomel electrode is -0.68 volt. Several commercial products have been analyzed with this method.

THE ORGANIC PHOSPHORUS COMPOUND currently known as Bayer L 13/59 (*O,O*-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate), as well as by the trade name Dipterex, was synthesized by Lorenz, Henglein, and Schrader (10). It is a condensation product of chloral and dimethyl hydrogen phosphite (7):



This compound has recently attracted wide interest in its use as an insecticide in various forms of fly baits (5, 7, 8) and possibly for the control of many other household and crop insects (2). However, the only reported analytical procedure for its estimation is the one described by Giang and Hall (6), which is based upon pyrolysis to split off chloroform and the development of a red color in aqueous pyridine by warming with alkali. This procedure may possibly be applied in the determination of Bayer L 13/59 in the small quantities present in plant residues, milk, or animal tissue extractives, but it is not suitable for use in the assay of technical materials. Consequently, reliable and sensitive methods of analysis are greatly needed for this new material in insecticide formulations. In view of the successful polarographic determination of chloral hydrate (3, 4) and other chlorinated aldehydes (3, 9), it was considered possible that Bayer L 13/59 could be determined by polarographic means.

#### Apparatus

The measurements were made with the Sargent pen-recording Model XXI polarograph. An H-cell with a saturated calomel electrode in the anode compartment was used, suspended in a water bath maintained at  $25^{\circ} \pm 0.5^{\circ}$  C. The capillary characteristics were:

$$m = 3.1 \text{ mg. per second, } t = 2.65 \text{ seconds per drop, and } m^{2/3}/t^{1/3} = 2.50 \text{ (at 0.0 volt).}$$

#### Reagents

Potassium chloride, 0.1*M*. Dissolve 7.456 grams of the salt (c.p. grade) in a liter of distilled water.

Gelatin, 0.1%. Dissolve 100 mg. of gelatin in water by heating, cool to room temperature, and make to 100 ml. with additional water. Make a fresh solution each day.

Nitrogen. Bubble through a portion of the test solution in a glass cylinder before passing through the sample solution.

Purified Bayer L 13/59. Recrystallize a technical material from petroleum ether containing a little benzene. Melting point, 78-80° C. (7).

#### Preparation of Standard Curves

Dissolve 1 gram of purified Bayer L 13/59 in water and make to 500 ml.

Pipet aliquots of 3, 5, 7, 10, 15, and 20 ml. into a series of 100-ml. volumetric flasks. To each flask add 20 ml. of the 0.1*M* potassium chloride and 2 ml. of the 0.1% gelatin and make to volume.

Transfer a portion of each of the test solutions to the sample compartment of the H-cell and deaerate with nitrogen gas for 10 minutes. Record the polarogram for each solution from 0 to -2.0 volts at sensitivities of 0.04, 0.06, and 0.08  $\mu$ a. per mm. with maximum damping. Plot the standard curves of wave height against milligrams of Bayer L 13/59 in 100 ml. of solution for each sensitivity.

#### Analysis of Fly Bait Formulations

For the analysis of fly bait formulations, weigh a sufficient amount of the sample and dissolve in water so that 1 ml. of the solution will contain approximately 1 mg. of Bayer L 13/59. Shake the solution intermittently for 1 hour and then centrifuge, if necessary. Pipet 20 ml. (or more) of the clear solution to a 100-ml. volumetric flask and proceed with the determination as described in the construction of the standard curves.

#### Results of Analysis

Four samples of technical Bayer L 13/59 were analyzed by the procedure above, employing samples of 20 to 30 mg. per 100 ml. The results are given in Table I. Baits and dusts of known

Bayer L 13/59 content prepared in this laboratory were analyzed and the results always indicated over 97% recovery. The results of analysis of three commercial formulations are given in Table II.

### Discussion

The polarograms for the technical materials were very similar to those for the purified Bayer L 13/59, with an observed half-wave potential of  $-0.68$  volt against the saturated calomel electrode. The standard curves of wave height against Bayer L 13/59 in the 100 ml. of solution were found to be straight lines, which, for the capillary and experimental conditions used, had slopes of 0.124, 0.186, and 0.248 mg. of Bayer L 13/59 per mm. of wave height for sensitivities of 0.04, 0.06, and 0.08  $\mu$ a. per mm., respectively.

Chloral hydrate, the major contaminant of the technical material, is reduced at a half-wave potential of  $-1.61$  volts and consequently does not interfere. *O,O*-dimethyl 2,2-dichlorovinyl phosphate (DDVP), a decomposition product of Bayer L 13/59 (77), is reduced at a half-wave potential of  $-1.53$  volts and does not interfere.

To further test the possible interfer-

**Table I. Percentage of Bayer L 13/59 in Technical Products**

Sample A	Sample B	Sample C	Sample D
94.6	97.3	96.7	97.7
94.4	97.7	96.6	98.2
94.8	97.2	96.8	97.8
Av.	94.6	97.4	96.7

**Table II. Percentage of Bayer L 13/59 in Commercial Formulations**

	Bait, %		
	1	2	10
	0.9	1.9	9.4
	1.0	1.9	9.6
	1.1	1.9	9.6
Av.	1.0	1.9	9.5

ence, a solution containing equal weights of chloral hydrate, DDVP, and Bayer L 13/59 was analyzed by this method. The presence of chloral hydrate and DDVP did not affect the polarographic wave for Bayer L 13/59.

This method has an accuracy of within  $\pm 2\%$ . Four milligrams of Bayer L 13/59 in 100 ml. of solution is apparently a minimum concentration for the sensitivities specified.

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## DIETARY CARBOHYDRATES

# A Review of the Effects of Different Carbohydrates on Vitamin and Amino Acid Requirements

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The literature on the effects of different carbohydrates on vitamin and amino acid requirements has been reviewed. A substantial body of evidence indicates that when a less soluble carbohydrate is substituted in the diet for a more soluble one, the requirements for most members of the vitamin B complex and for essential amino acids, reported as a percentage of the diet, decrease. The effect of complex carbohydrates in lowering vitamin B requirements has been related to changes in the intestinal microflora; however, there is no evidence to suggest that such changes influence amino acid requirements. Instead, the lower amino acid requirements appear to be a result of physiological effects on food intake, digestion, or absorption. Thus, although dietary carbohydrate serves primarily as a source of calories, indirect effects of individual carbohydrates may be of considerable nutritional significance.

ALMOST 60 years ago, before it was known that there were such important dietary accessories as vitamins and before the concept of indispensable amino acids had evolved, Eijkman (72) noticed that hens, which developed polyneuritis when fed largely on polished rice, did not do so when the rice was replaced by potato starch. Although the significance of this observation could not be appreciated at the time, it now appears to have been the first hint that

vitamin requirements can be modified by the nature of the dietary carbohydrate.

Somewhat later, between 1923 and 1927, after the term vitamin had been coined, Randoin and Simonnet (57) published a series of papers in which they reported that the nature of the carbohydrate in the diet influenced the rapidity with which the symptoms of "vitamin B" deficiency developed in pigeons. They also noted that the relatively indi-

gestible potato starch exerted the most pronounced protective effect. Between 1926 and 1928, Fredericia in Denmark (75), and Roscoe (59) and Kon and Watchorn in England (38) described the phenomenon of refection in which rats that had lost weight after being fed on a diet deficient in the vitamin B complex and containing uncooked starch, spontaneously resumed growth. Fredericia and associates (76) originally observed that refection occurred only occasionally