QUANTITATIVE DETERMINATION OF DIMETHYL CHLOROVINYL PHOSPHATE BY ALTERNATING CURRENT POLAROGRAPHY

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Dimethyl chlorovinyl phosphate (DDVP),

$$\left[\begin{matrix} CH_3O \\ CH_3O \end{matrix} \!\!>\!\! P(=O) - O - CH = CCl_2 \right],$$

is used as an insecticide in agriculture. A method used in the USA for the quantitative determination of DDVP is based on estimation of the chlorine with the aid of sodium diphenyl [1], but this reagent is not available here. A method based on iodometric titration of the dichloroacetaldehyde, formed by hydrolysis of DDVP with alkali, gave good results only with the pure product and was not applicable to determinations in the presence of other chlorine derivatives. A method of quantitative analysis by means of infrared spectroscopy has also been developed [2].

We showed previously that DDVP was not reduced at a dropping mercury electrode [3, 4]. Attempts were made to develop a method of quantitative determination based on bromination of the double bond in DDVP. However, the bromination reaction proceeded slowly and did not go to completion. Moreover, it was found that the end product of the bromination of DDVP was not reduced at a mercury electrode up to a potential of −2.3 V.

Phosphate groups in organic compounds may be determined by means of their absorption peaks. When organic compounds are adsorbed, both alternating current polarograms and curves relating differential capacity to potential show two peaks, corresponding to the processes of adsorption and desorption of molecules. The peak current shown on the alternating current polarogram, for a range of dilute solutions, is proportional to the volumetric concentration of the substance [5] and can therefore be used for quantitative analysis.

Investigation of the adsorption of carefully purified DDVP, in M KCl as supporting electrolyte, by means of a vector polarograph, showed that there were two peaks on the alternating current polarograms (Fig. 1). The height of the first peak was greater than that of the second. The potentials, corresponding to the peak maximum currents, shifted slightly with increasing concentration. The first peak shifted to a more positive potential and the second to a more negative potential. With both peaks there was a linear relation between peak height and concentration (Fig. 2).

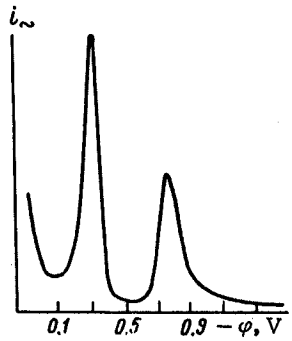

Fig. 1. Vector polarogram of 10^{-3} M DDVP in M KCl as supporting electrolyte.

Vector polarograms were recorded for all the impurities, isolated by thin layer chromatography, and it was found that these were inactive from the point of view of polarography or adsorption. The only electrically active impurity was chlorofos, which under certain conditions showed a peak at a potential of −0.75 V. It is clear from Fig. 3, which shows a vector polarogram for an artificial mixture of 10^{-3} M DDVP and 10^{-3} M chlorofos, that the height of the second peak was considerably greater than in the case of 10^{-3} M DDVP alone. There was a small step on the curve at a potential close to −0.75 V. In this case the second peak represented the sum of the reduction peak of chlorofos and the desorption peak of DDVP. Measurements, carried out with artificial mixtures of DDVP and various concentrations of chlorofos, showed that the height of the first peak did not

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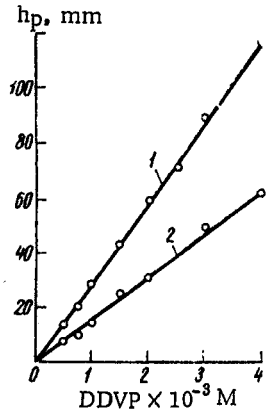

Fig. 2. Relation between peak height and DDVP concentration: 1) for the first peak at E = −0.3 V; 2) for the second peak at E = −1.1 V.

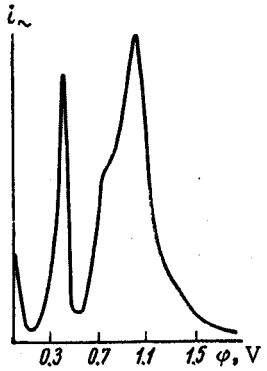

Fig. 3. Vector polarogram of an artificial mixture of 10^{-3} M DDVP and 10^{-3} M chlorofos, with M DCl as supporting electrolyte.

depend on the presence of chlorofos and could therefore be used for determination of DDVP in the technical product.

The method was checked with artificial mixtures. When the chemically pure grade of reagent was used with distilled water, the lower limit of detection for DDVP was 0.02 mg/ml. Since the alternating current polarograph is very sensitive to traces of metal cations, it is important to pay great attention to the purity of the reagents and the water in the determination of small amounts of DDVP.

The relative error, for the determination of DDVP in the concentration range 10^{-3} to 5×10^{-3} M, was ±2%, and increased to ±5% for the determination of small quantities. The time taken for an analysis was 25 to 30 min.

The work was carried out with a TsLA vector polarograph. A dropping mercury electrode was used with a drop time of 4.2 sec. The mercury pool at the bottom of the cell served as the anode. A saturated silver chloride electrode was used for reference when a three-electrode system was employed. The solvent was distilled water. Oxygen was removed from the solutions by passage of nitrogen containing less than 0.2% O_2. Chemically pure grade KCl was used for making up the supporting electrolyte.

When a DDVP vector polarogram was recorded, the delay time was selected such that it was 70 to 80% of the mercury electrode drop time at E = −1.2 V. The rate of application of potential should not exceed 5 mV/sec, with an alternating voltage amplitude of 4 mV. The sensitivity of the instrument should be selected such that the maximum concentration used in constructing the calibration curve gave a first peak height of 150 to 170 mm.

The purity of the reagents and water were checked by recording vector polarograms for solutions of the supporting electrolyte, freed from oxygen, at a sensitivity of $^1/_2$. If there were no electrically active impurities in the solution, then the vector polarogram was a straight line.

In order to construct a calibration curve, the following weights: 0.0088, 0.0176, 0.0264, 0.0352, and 0.0440 g, of carefully purified DDVP were weighed out to a precision of 0.2 mg and dissolved in M KCl. These weights corresponded to 20, 40, 60, 80, and 100% contents of DDVP in solution. Nitrogen was passed through the solutions, curves were recorded, and peak heights were measured at E = −0.3 V to construct a calibration curve.

To carry out an analysis, 0.0440 g of sample was dissolved in M KCl solution in a 100 ml graduated flask. A portion of the solution was transferred to the polarographic cell and nitrogen was passed through it for 15 min. Then the vector polarograph was set to the selected retention time, amplitude of alternating voltage, sensitivity, and scanning rate, and a vector polarogram was recorded. The peak height at E = −0.3 V was measured, and the concentration of DDVP was obtained from the calibration curve. In order to increase the precision it was recommended that two determinations should be made in parallel and that two vector polarograms should be recorded for each solution. The final result was then the arithmetic mean of the four determinations.

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