The Determination of Dimexan in Crops

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Residues of Dimexan on vegetables and other crops can be determined by treating the sample with ethanolic sodium hydrosulphide, then boiling with dilute sulphuric acid and absorbing the CS_2 evolved in a modified Viles' reagent. The colour developed is measured spectro-photometrically. With onions, high results were obtained in recovery tests unless the onions were fresh and examined at once.

The substance known as Dimexan in Gt. Britain (Dimexano in Europe) is bis-(methyl-xanthic) disulphide, $CH_3O–\overset{\overset{\|}{S}}{C}–S–S–\overset{\overset{\|}{S}}{C}–OCH_3$. It is used as a haulm-killer and defoliant.

At ordinary summer temperatures in Britain it is a fairly volatile oil. The crops referred to in this report were sprayed with the proprietary preparation "Tri-P.E.", consisting of an emulsifiable concentrate containing about 40 per cent. of dimexan, and made by Fabriek van Chemische Producten, Vondelingenplaat N.V., of Rotterdam.

The method employed for the determination of Dimexan is an adaptation of a method, first published by Clark[1] and improved by Cullen[2], for the determination of residues of dithiocarbamates. These substances yield carbon disulphide (CS_2), on treatment with acids, whereas Dimexan requires preliminary treatment with ethanolic sodium hydrosulphide. The reactions are as follows—

$$CH_3O{\cdot}CS{\cdot}S_2{\cdot}CS{\cdot}OCH_3 + 2NaSH \rightarrow 2CH_3O{\cdot}CS{\cdot}SNa + H_2S + S$$
$$CH_3O{\cdot}CS{\cdot}SNa + H^+ \rightarrow CH_3OH + Na^+ + CS_2$$

A stream of nitrogen is passed through the apparatus and carries with it the evolved gases, first through a solution of zinc acetate to remove the H_2S and then into a modification of Viles' reagent[3]—cupric acetate and diethanolamine in ethanol—which reacts with the CS_2 to form yellow chelates[2]. The optical density of the solution is measured spectro-photometrically. This method was first devised in the Vondelingenplaat Laboratories, but various improvements were made in the Norwich laboratory and all the analyses referred to in this paper were made in Norwich.

Apparatus

This is shown in Figure 1. A litre flask with three necks has a condenser fitted vertically to the middle neck, the two side necks being used for the

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admission of nitrogen and for the addition of liquids *via* a dropping funnel fitted with a stop-cock. From the top of the condenser, a tube leads the issuing gases through two gas-washing tubes (which absorb the H_2S present) and then through a sintered glass gas distributor (porosity 2) in the final absorption tube which contains the modified Viles' reagent. Each absorption tube to be used in this position is calibrated by measuring into it 5·0 ml of water with an accurate pipette and marking the level reached by the water. It is important that the internal diameter of this tube should be only 2–3 mm more than that of the gas distribution tube (the authors' pattern has a maximum external diameter of 13 mm), so that the latter is immersed in as great a depth as possible when 5 ml of the modified Viles' reagent is introduced. To use a larger volume of reagent would result in a loss of sensitivity, and for the same reason the reagent is not diluted before determining the optical density, as is done in Cullen's method[2]. The volume of 5 ml (less drainings) is ample for use in a 10-mm spectrophotometer cell. All joints are standard glass cones and sockets or spherical joints, introduced to obtain some degree of flexibility.

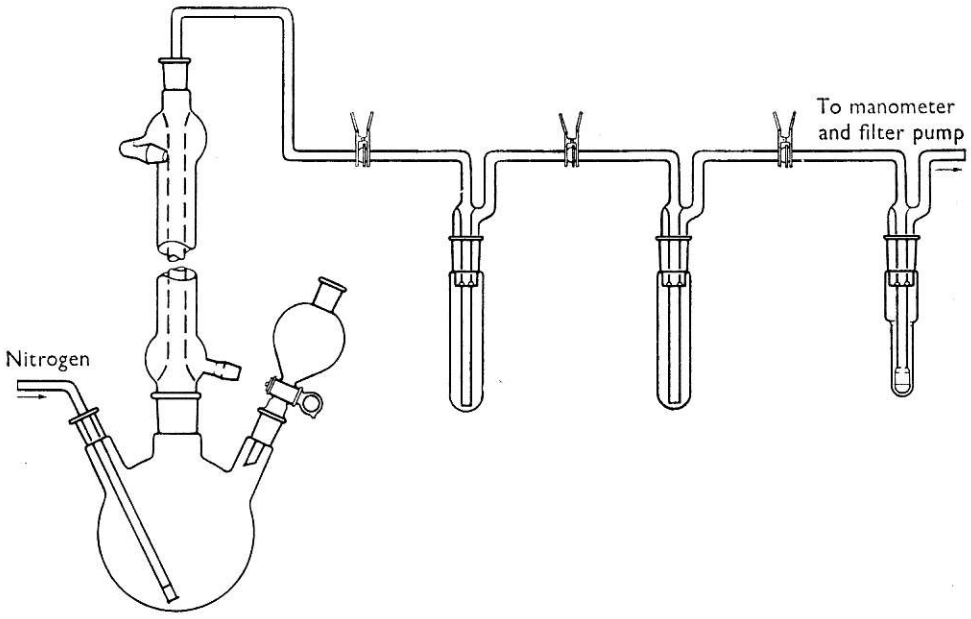

Fig. 1

Reagents

1. *Industrial Methylated Spirit:* I.M.S., 74 degrees o.p.
2. *Sodium Hydrosulphide Solution:* 5 per cent. in I.M.S. Dissolve 6·6 g of sodium hydrosulphide, $NaHS.H_2O$, (Fluka A.G. Buchs, Switzerland) in I.M.S., filter and make up to 100 ml. (Alternatively, dissolve 22 g of sodium sulphide, $Na_2S.9H_2O$, in a minimum amount of water in a 100-ml

volumetric flask. Add I.M.S. to a total volume of about 80 ml and cool nearly to 0° C in ice. Add, gradually and with constant swirling, 17·8 ml of cooled, 5 N hydrochloric acid solution. Allow the mixture to come to room temperature, make up to 100 ml with I.M.S. and mix well. A precipitate may form; always use the clear solution and discard it after one week.)

3. *Zinc Acetate Solution:* 10 per cent. w/v.
4. *Sulphuric Acid:* 5 N H_2SO_4 soln.
5. *Viles' Reagent (Modified):* Dissolve 10 mg of cupric acetate monohydrate and 25 g of diethanolamine in I.M.S. and dilute with I.M.S. to 250 ml. 5 ml of this reagent are suitable for the absorption of at least 200 μg of CS_2, which is equivalent to about 280 μg of Dimexan, or 2·8 p.p.m. on a 100-g sample.

Method

Introduce into the three-necked flask a weighed sample (usually 100 g) of the plant material to be examined. Add 50 ml of I.M.S. and 2 ml of sodium hydrosulphide solution; swirl for one minute, connect the flask to the condenser and allow to stand for 15 minutes. Into each H_2S trap introduce 12 ml of zinc acetate solution, and pipette 5·0 ml of Viles' reagent into the final absorption tube. With the apparatus completely assembled, turn on the nitrogen and apply slight suction from the vacuum pump, adjusting both so that with a reasonable flow of nitrogen as shown by the bubbles in the traps, a slight negative pressure is shown on a manometer, to reduce risk of loss of gas (and therefore of CS_2) at the spherical joints. Add, from the dropping funnel, 50 ml of water followed by 50 ml of 5 N sulphuric acid, and after nitrogen has been passing for three to four minutes, heat the contents of the flask to boiling point and boil for 30 minutes. The flow of nitrogen must be adjusted so that frothing in the first H_2S trap is controlled; the rate of bubbling may have to be restricted to 2 to 3 bubbles per second until boiling begins but can be increased towards the end of the boiling period, when the frothing has died down, in order to ensure that all CS_2 has been carried through to the final absorption tube. The contents of the second H_2S trap should remain clear throughout the determination, indicating that all H_2S has been absorbed in the first trap.

At the end of the 30-minute boiling period, disconnect the final absorption tube and rinse the gas distributor into it with the few drops of I.M.S. necessary to restore the volume of the contents to the 5-ml mark. Mix, and allow to stand for 15 minutes. (Disconnect the H_2S traps and open the top of the dropping funnel before turning off the flame and the nitrogen.) Determine the optical density of the contents of the absorption tube in a 1-cm cell at 435 mμ, with Viles' reagent (as modified) in the reference cell.

NOTES

1. Dimexan residues will be present on, rather than in, the crop, and as with the dithiocarbamates, there is danger of decomposition if the crop is cut or mashed and the dimexan comes into contact with water, enzymes, etc. before the I.M.S. and the sodium hydrosulphide are added. For this reason the crop is handled as little as possible; peas are shelled and weighed out whole, beetroot is cut up into cubes small enough to enter the neck of the reaction flask but no smaller, and so on.
2. Zinc (or cadmium) acetate solution is better than lead acetate solution in the H_2S traps because the tubes are easier to clean afterwards, the precipitated sulphide dissolving readily in hydrochloric acid.
3. The volume of sodium hydrosulphide solution used (2 ml) is theoretically in large excess of the amount required to react with any amount of Dimexan likely to be met with; 1 ml would probably be sufficient. If more than 2 ml are used, zinc sulphide may appear in the second H_2S trap, destroying the analyst's conviction that no H_2S is reaching the Viles' reagent.

Calibration Graph

A calibration graph is constructed for each crop to be examined, by adding to 100-g portions of the crop (free of Dimexan) known amounts of standard Dimexan solution from zero upwards. It was found convenient to use 0, 25, 50, 75 and 100 μg amounts of Dimexan solution, corresponding to 0, 0·25, 0·5, 0·75 and 1·0 p.p.m. respectively. Under the conditions described, using a Unicam SP 500 spectrophotometer, the optical density corresponding to 100 μg of Dimexan was 0·66. The "blank" using 100 g of untreated material, was satisfactorily low; for example, with peas the optical density was 0·02 to 0·04. It was found that the relation between weight of Dimexan and optical density was linear up to 100 μg, the highest amount which was to be determined.

Abnormal Results

Analyses of shelled peas and of red beet at intervals of one to seven days after spraying were made, using as control samples, peas and beet from parts of the same field that had been left unsprayed. The results were in accordance with expectation and exhibited no unusual features; determinations on triplicate samples from different parts of the sprayed area on any one day were in satisfactory agreement with each other and the "blanks" on the control samples were low (optical density 0·02 to 0·04). When known amounts of Dimexan were added to portions of sprayed peas, the Dimexan content of which had already been determined, the recovery of the added Dimexan was 95 per cent. or better.

Analyses of onions, however, gave unusual results. Whereas red beet, two days after spraying, had been found to contain less than 0·5 p.p.m. of Dimexan,

onions two days after spraying were found to contain 1·3 to 1·8 p.p.m. The "blanks" on control samples were low (optical density 0·03 to 0·05) but when recovery tests were made in duplicate two days later, adding 50 μg of Dimexan to control samples, recoveries of 77 and 75 μg were unexpectedly obtained.

This clearly required to be looked into further; the control onions had been chopped up 2 days before the recovery tests were made and might have decomposed with formation either of CS_2 or of some compound that behaved similarly towards Viles' reagent. Accordingly, some unsprayed onions that had been lying in the field for 7 days were obtained and chopped up; blanks and recovery tests were made immediately. The blank was a little higher than before (optical density 0·065) and the apparent recovery was 114 per cent.

Three pounds of onions were then purchased from a local shop. They were "topped and tailed", then chopped up into cubes as before. Three Kilner jars were filled and kept under various conditions (see below); "blank" and recovery tests were then made. The results are shown in the following table:

TABLE I

APPARENT RECOVERY OF DIMEXAN FROM ONION SAMPLES

	Sample		Sample plus 50 μg of Dimexan		
	Date of Testing	Optical Density	Date of Testing	Optical Density	Recovery *per cent.*
Examined on day of preparation	14 Sept.	0·027	14 Sept.	0·370	101
Jar kept in deep-freeze for 4–5 days	18 Sept.	0·059	19 Sept.	0·415	114
Jar kept at room temperature for 4–5 days ..	18 Sept.	0·029	19 Sept.	0·432	119
Mean control optical density		0·038			

Although the variability in the "blanks" as shown by the figures in Table I is rather large and prevents any firm conclusion from being drawn, the matter seems to warrant further investigation. If onions are being examined for Dimexan, both the sprayed and the unsprayed samples should be examined on the day on which they are taken.

References

1. Clark, D. G., *et al.*, *Anal. Chem.*, 1951, **23**, 1842.
2. Cullen, T. E., *Anal. Chem.*, 1964, **36**, 221.
3. Viles, F. J., *J. Ind. Hyg. Toxicol.*, 1940, **22**, 188.