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Determination of Chloro-2-methylphenoxyacetic Acid by Infrared Spectrophotometry

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In 1941, Slade, Templeman and Sexton[1] found that 4-chloro-2-methylphenoxyacetic acid was very useful as a weedkiller. This product has found very extensive use especially in England, where it has been marketed by ICI under the trade names "Methoxone" and "Agroxone". It has also been widely used in many other countries including Sweden. The product is now made by many manufacturers and is generally called 4K2M.

The technical 4K2M is not a pure product and is usually sold dissolved in water as the sodium salt. It contains, in consequence of the preparation method [see *e. g.* Swedish patent no. 126 571[2]], in addition to 4-chloro-2-methylphenoxyacetic acid, varying amounts of the isomeric 6-chloro-2-methylphenoxyacetic acid, unchlorinated 2-methylphenoxyacetic acid and the higher chlorinated 4,6-dichloro-2-methylphenoxyacetic acid.

No method for the analysis of this mixture has been found in the literature. The task is not an easy one. It would be very difficult to find a chemical method for the analysis of the two isomers, 4-chloro-2-methylphenoxyacetic acid and 6-chloro-2-methylphenoxyacetic acid, because they can be anticipated to show very much the same chemical behavior. The physical properties, however, ought to be more suitable for the determination, but the presence of the two other components, the unchlorinated and the dichlorinated acid, makes the analysis difficult. It is not possible to employ isolated measurements of such physical properties as melting point or index of refraction for the analysis of the mixture. A method must be found by which data for each one of the components in the mixture can be determined.

Under these circumstances it seems reasonable to investigate the possibility of analyzing the mixture by spectrophotometric measurements in infrared

The conditions necessary for these measurements are that characteristic and not to closely located absorption bands can be found for the different substances. No investigations on the light absorption in infrared of chloro-2-methylphenoxyacetic acids seem to have been published.

The purpose of this work was to prepare the four compounds 2-methylphenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid, 6-chloro-2-methylphenoxyacetic acid and 4,6-dichloro-2-methylphenoxyacetic acid and to investigate their light absorption in infrared light. If possible a method for the determination of the four compounds would be worked out by spectrophotometrical means.

MATERIALS

2-Methylphenol: The crystalline *o*-cresol had a minimum melting point of 30.3° C.

4-Chloro-2-methylphenol: *o*-Cresol was chlorinated with sulphurylchloride as described by Sah and Anderson[4]. The reaction mixture was washed with sodium carbonate solution and water and dried with calcium chloride. During the following fractional distillation in vacuum, it was necessary to admit nitrogen through the capillary. Air caused a certain decomposition. Melting point 48.6—49.2° C.

6-Chloro-2-methylphenol: *o*-Cresol was chlorinated with chlorine at about 75° C and fractionated in vacuum. The first fraction containing 6-chloro-*o*-cresol and a small amount of unchanged *o*-cresol with almost the same boiling points was transformed into the corresponding acetates by Nord[5]. These acetates could be separated by distillation on account of a great difference in boiling point. The pure 6-chloro-2-methylphenyl acetate was hydrolysed to 6-chloro-2-methylphenol, which was further purified by recrystallization. Melting point 1.0—1.4° C.

4,6-Dichloro-2-methylphenol: This compound has almost the same boiling point as 4-chloro-2-methylphenol and therefore it cannot be prepared in pure form by chlorination of *o*-cresol. Pure 6-chloro-2-methylphenol was underchlorinated and 4,6-dichloro-2-methylphenol was obtained by distillation of the reaction mixture. It was purified by crystallization from petroleum ether. Melting point 52.5—52.7° C.

The corresponding phenoxyacetic acids were prepared by reaction of the phenols in alkaline solution with monochloroacetic acid in 30 % excess. The monochloroacetic acid was purified by recrystallization from glacial acetic acid, and was found free from dichloroacetic acid[6]. The reaction mixture was about $2N$ with respect to the phenols and the reaction temperature was kept at about 100° C. After complete reaction, the mixture was acidified to pH 7.0 and nonreacted phenol was extracted with ether. The solution was then acidified to complete precipitation of the acid which was extracted with ether and purified by recrystallization from benzene or chlorobenzene. Analysis data and melting points of the acids are shown in Table 1. The melting points were determined in accordance to Hershberg[7].

APPARATUS

A Beckman IR 2 Infrared Spectrophotometer with rock salt prism was used for the measurements in infrared. The recorder had been connected to an electrical compensation apparatus made in accordance to specifications by Foreman and Jackson[8]. The

Table 1. Analyses and melting points.

Compound	Elementary analyses						Melting point °C
	C %		H %		Cl %		
	calc.	found	calc.	found	calc.	found	
2-Methylphenoxyacetic acid	65.05	64.98	6.07	6.13	—	—	154.8—154.9
4-Chloro-2-methylphenoxyacetic acid	53.88	53.66	4.52	4.53	17.68	17.69	120.0—120.2
6-Chloro-2-methylphenoxyacetic acid	53.88	53.78	4.52	4.46	17.68	17.69	109.5—109.8
4,6-Dichloro-2-methyl-phenoxyacetic acid	45.98	45.87	3.43	3.36	30.17	30.30	187.9—188.2

determinations were made as follows. First the spectrum for solvent and cell was recorded. The paper was now reset to the starting point. The same cell was filled with the solution and the spectrum recorded. In doing so the spectrum of the solvent was followed by a horizontally movable pointer connected to the compensation apparatus. The recorded curve was the spectrum of the dissolved compound.

ABSORPTION CURVES

The selection of a solvent for infrared absorption measurements raised difficulties. The acids are almost insoluble in hexane and pentane. Carbon tetrachloride and carbon disulphide were not very suitable (Table 2).

Table 2. Solubility of 2-methylphenoxyacetic acid.

Compound	Solubility of 2-methylphenoxyacetic acid g/liter solvent
Carbon tetrachloride	0.50
Carbon disulphide	0.22
Chloroform	12.80
2-Nitropropane	10.04

From Table 2, it is evident that chloroform and nitropropane are better solvents. Such solvents as acetone, cyclohexanone and methylal are even better.

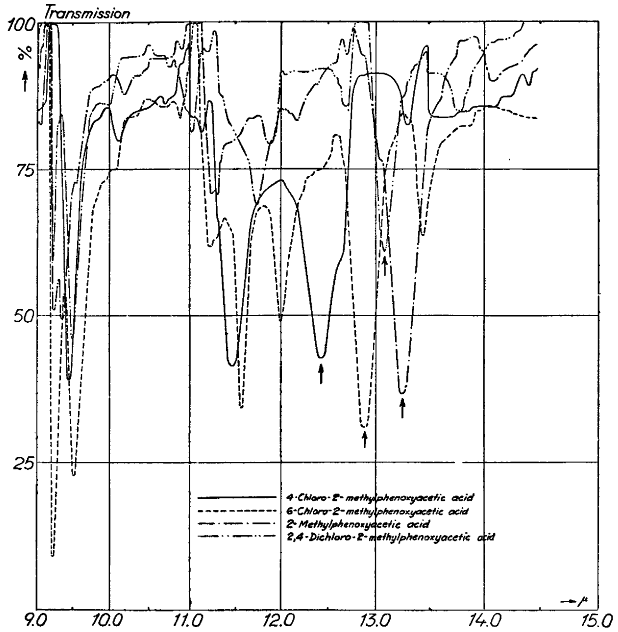

Fig. 1. Absorption curves of the acids.

Between 5—9 μ no measurements could be made because the solvents used had too high an absorption compared to the dissolved acids. Chloroform had the lowest absorption within this region, but its dissolving power for 2-methylphenoxyacetic acid and 4,6-dichlorophenoxyacetic acid was too low to make analysis possible.

Between 9—15 μ the absorption curves were recorded with acetone as a solvent. A 0.1 mm cell was used and the concentration for 4-chloro- and 6-chloro-2-methylphenoxyacetic acids was 90 g/liter. Owing to the lower solubility of 2-methylphenoxyacetic acid and 4,6-dichloro-2-methylphenoxyacetic acid, it was only possible to use a concentration of 45 g/liter. The obtained absorption curves are shown in Fig. 1.

Within this region there are no completely undisturbed absorption maxima. It is, however, possible to select maxima suitable for an analysis of the four mixed acids. These maxima are indicated by arrows in Fig. 1 and their wave lengths are as follows:

Table 3. Absorption maxima.

Compound	Wave lengths
4-Chloro-2-methylphenoxyacetic acid	12.38
6-Chloro-2-methylphenoxyacetic acid	12.86
4,6-Dichloro-2-methylphenoxyacetic acid	13.05
2-Methylphenoxyacetic acid	13.22

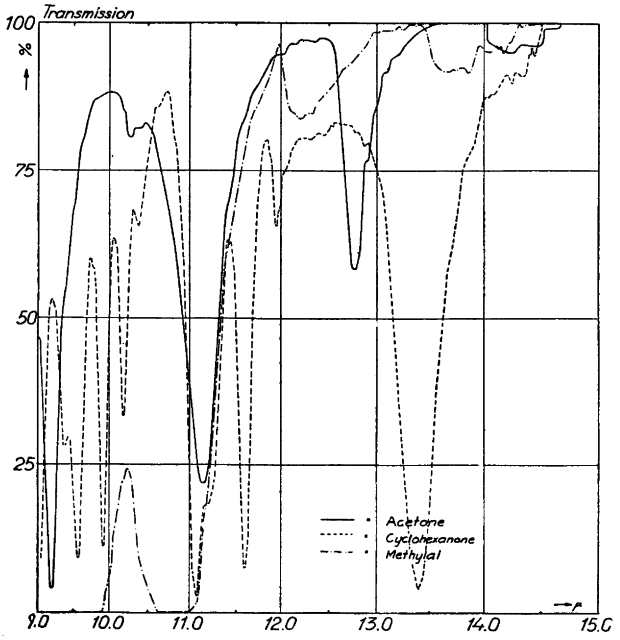

Fig. 2. Absorption curves of the solvents.

The absorption curves between 9—15 μ for acetone, cyclohexanone and methylal were recorded (Fig. 2).

Cyclohexanone had too high an absorption within the region 12.38—13.22 μ to be useful as a solvent. Methylal had a slight absorption but it was less suitable for quantitative measurements because of the low boiling point 42—43° C. Therefore we used acetone.

Acetone shows an absorption maximum at 12.75 μ which interferes with the determination of 6-chloro-2-methylphenoxyacetic acid but its extinction at the other wavelengths is comparatively low.

ANALYTICAL PROCEDURE

A number of solutions of each one of the four acids were prepared in different concentrations in acetone. The extinctions were determined at the four wavelengths recorded in Table 4. The same rocksalt cell of about 0.1 mm length was used for all determinations on solutions and solvents. In diagrams drawn on millimeter paper 450 × 600 mm, we could plot for each wavelength the extinctions of the four acids as a function of their concentrations (Fig. 3). In these diagrams the following abbreviations have been used: 2-methylphenoxyacetic acid 2M; 4-chloro-2-methylphenoxyacetic acid 4K2M; 6-chloro-2-methylphenoxyacetic acid 6K2M and 4,6-dichloro-2-methylphenoxyacetic acid 46K2M.

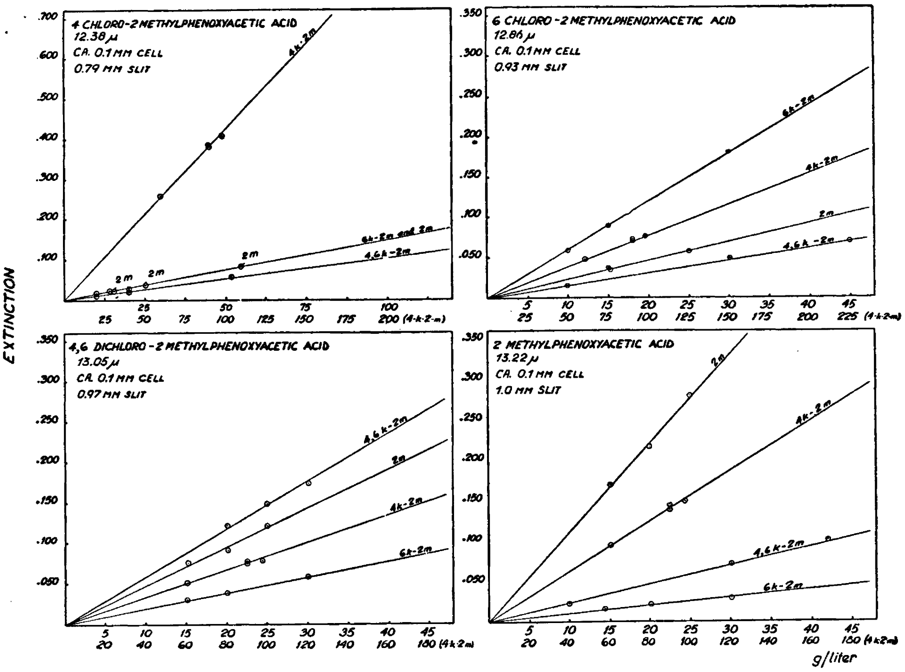

Fig. 3. Working curves.

The diagrams show a linear relationship indicating the validity of Beer's law:

$$E = \log I_0/I = K \cdot c \cdot l$$

where E = extinction, I_0 = light transmitted by the pure solvent, I = light transmitted by the solution, K = extinction coefficient of absorbing material, c = concentration in grams per liter and l = lengths, of solution path in centimeters.

The extinction coefficients of the four acids at each one of the four wavelengths can be calculated from values obtained in the concentration diagram. After determination of the extinction of a solution of the four acids in the same cell at the different wave lengths four equations of the following type are obtained.

$$E = K_1c_1l + K_2c_2l + K_3c_3l + K_4c_4l$$

With these equations the concentrations c_1, c_2, c_3 and c_4 of the four acids can be calculated. We have used a method of solving the equation system by successive approximations described by Daasch [9].

Table 4. Analyses of known mixtures.

Sample	2-Methylphenoxyacetic acid %		4-Chloro-2-methylphenoxyacetic acid %		6-Chloro-2-methylphenoxyacetic acid %		4,6-Dichloro-2-methylphenoxyacetic acid %		Total % found
	calc.	found	calc.	found	calc.	found	calc.	found	
1	0	0	90.1	91.0	5.0	4.4	4.9	4.9	100.3
2	5.0	5.3	77.6	77.0	11.2	10.0	6.2	6.6	98.9
3	4.0	3.5	59.4	60.4	29.7	29.7	6.9	7.8	101.4
4	35.0	35.4	45.0	45.0	20.0	20.0	0	0	100.4

EXPERIMENTAL RESULTS

A number of mixtures with varying known amounts of the four acids were dissolved in acetone (50—100 grams per liter, total) and analysed as described. The results are given in Table 4.

The accuracy obtainable depends on the reproducibility of the transmittance measurements. The wavelength of 6-chloro-2-methylphenoxyacetic acid must be set very carefully because it is on the side of the acetone (solvent) band.

With extinction measurements within the used range ($E = 0.3$—0.5), it is possible to reach a reproducibility of $\pm$ 0.02 with careful work. This means a maximum average error in the determination of $\pm$ 1.5 units in the calculated percentage. However, the error is generally considerably less which appears from the results obtained with mixtures of known composition.

We have analysed some of the commercial 4K2M preparations available in Sweden 1949. All of them were solutions and the acids were extracted as follows:

A 150 ml sample is acidified with hydrochloric acid to pH 7.0 and the liberated cresols extracted with 40 ml of ether. The pH in the extracted solution must not be higher than 8.0, if so more acid is added before separation. The solution is then extracted once more with 40 ml of ether. The solution which is now free from cresols is acidified with hydrochloric acid until precipitation is complete and the precipitate extracted twice with 40 ml of ether. The ether extract is washed twice with 25 ml of water, evaporated on a steam bath and dried at 110° C.

The found compositions of the different samples of 4K2M are shown in Table 5.

Table 5. Analyses of technical 4K2M.

Sample	2-Methyl-phenoxy-acetic acid %	4-Chloro-2-methyl-phenoxy-acetic acid %	6-Chloro-2-methyl-phenoxy-acetic acid %	4,6-Dichloro-2-methyl-phenoxy-acetic acid %	Total %	Chlorine content %	
						Calculated from infrared analyses	Determined according to Carius
1	4	61	26	8	99	18.4	18.29
2	10	74	12	3	99	16.3	16.01
3	4	62	23	9	98	18.1	18.29
4	52	32	6	2	92	7.4	7.73

The deficit of 8 per cent found in sample 4 indicates that unknown components are also present in this product.

SUMMARY

The four compounds 2-methylphenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid, 6-chloro-2-methylphenoxyacetic acid and 4,6-dichloro-2-methylphenoxyacetic acid have been prepared in very pure form, and their light absorption in infrared has been determined. The infrared region revealed suitable absorption maxima. A procedure for quantitative analysis has been worked out. This procedure has been successfully applied to the analysis of mixtures of the pure acids. A number of commercial products of chloro-2-methylphenoxyacetic acids have been analysed.

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