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The Determination of Chlorinated *o*-Cresols and Chlorinated *o*-Toloxyacetic Acids

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Methods for the determination of mixtures of chlorinated *o*-cresols by infrared spectroscopy or by partition gas cromatography are described. Chlorinated *o*-toloxyacetic acids are determined as the corresponding chlorinated *o*-cresols after splitting by means of pyridine hydrochloride.

By the chlorination of *o*-cresol a mixture of 4-chloro-, 6-chloro-, 4,6-dichloro-*o*-cresol and unchlorinated *o*-cresol is obtained. The boiling points of these compounds are shown in Table 1.

A distillation will give a low boiling fraction containing *o*-cresol and 6-chloro-*o*-cresol. These two compounds are inseparable by distillation because of their close boiling points. The higher boiling fraction of 4-chloro-*o*-cresol and 4,6-dichloro-*o*-cresol can be resolved by distillation only with great difficulty. Such fractionation is therefore of little use in the analysis of chlorinated *o*-cresols.

In agreement with Freeman, Gardner and Pound [3] it was found that the ultra-violet absorption spectra of the four cresols are too similar to be used for a direct analysis. Much more useful are the infra-red absorption spectra as shown in Figs. 1–4.

By use of suitable absorption maxima the chlorinated *o*-cresols could conveniently be determined by spectrophotometric analyses. Details of the analyses are given in Table 2.

Table 1. The boiling points of *o*-cresol and chlorinated *o*-cresols.

Compound	Boiling point °C/mm Hg
o-Cresol	191/760
6-Chloro-*o*-cresol	191.0–192.3/757 [1]
4-Chloro-*o*-cresol	225/760 [2]
4,6-Dichloro-*o*-cresol	231.6–231.9/739 [1]

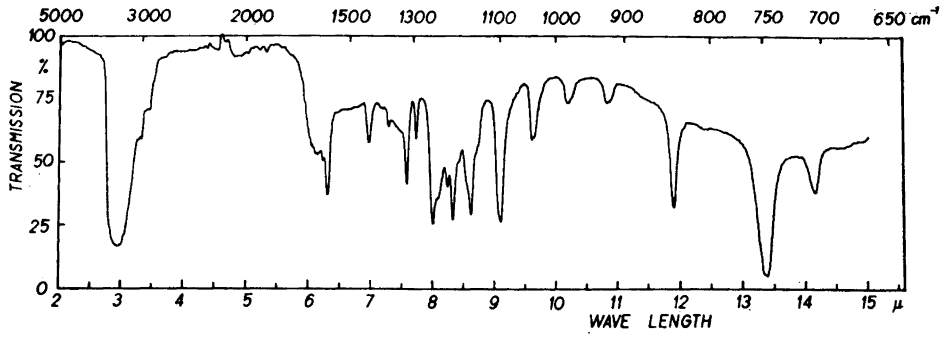

Fig. 1. The infra-red spectrum of *o*-cresol in CS_2-solution.

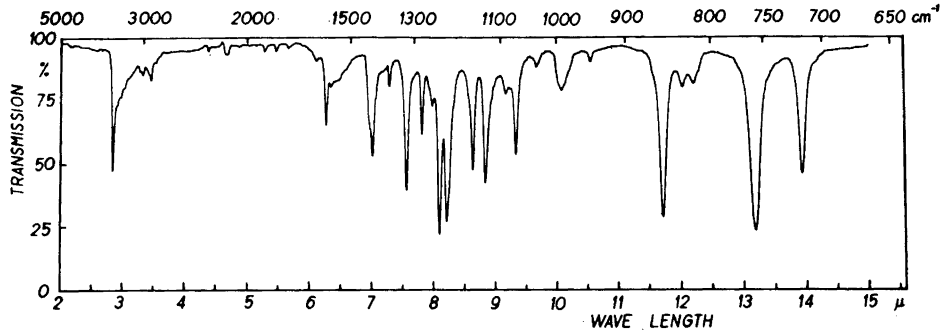

Fig. 2. The infra-red spectrum of 6-chloro-*o*-cresol in CS_2-solution.

The interference of the other compounds at each of these wave-lengths is not very high. It is, however, necessary to prepare a number of solutions of the four cresols in different concentrations and to determine the extinctions at the four wavelengths given in Table 2. In diagrams drawn on millimeter paper the extinctions of the four cresols for each wavelength are plotted as a function of their concentrations [4,5]. By means of these working curves the composition of other samples of these cresols can easily be calculated from the obtained extinction data.

Table 2. Spectrophotometric determination of chlorinated *o*-cresols. Conc. 0.015 g/ml CS_2; Cell 0.4 mm.

Compound	Wave length μ
o-Cresol	13.35
6-Chloro-*o*-cresol	8.80
4-Chloro-*o*-cresol	12.46
4,6-Dichloro-*o*-cresol	13.71

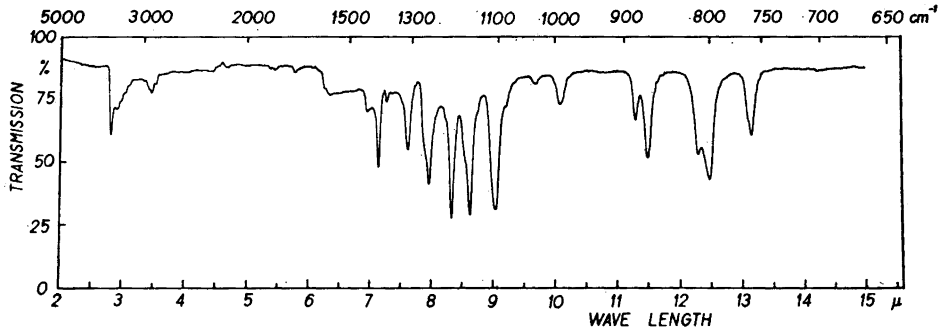

Fig. 3. The infra-red spectrum of 4-chloro-*o*-cresol in CS_2-solution

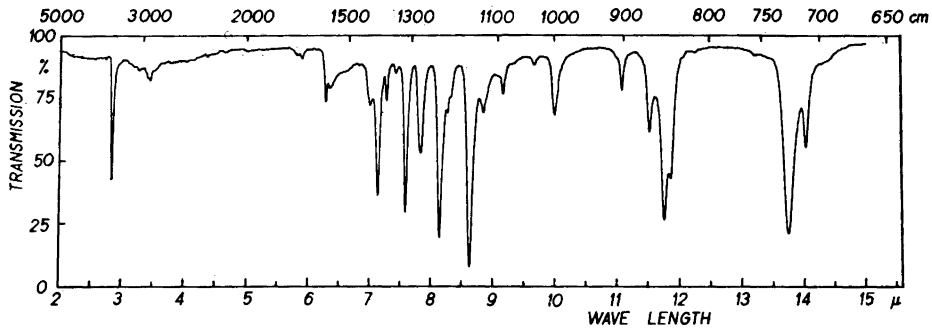

Fig. 4. The infra-red spectrum of 4,6-dichloro-*o*-cresol i CS_2-solution.

This spectrophotometric analytical method has, during a number of years' been used successfully at the Electrochemical Plant, Skoghallsverken, Skoghall, during the manufacture of 4-chloro-*o*-cresol.

For the analysis of chlorinated *o*-cresols partition gas cromatography was also found to be very useful. With a Perkin Elmer Fractometer 116 and Perkin Elmer Standard Packing A in the column the following retention volumes were obtained (Table 3).

Table 3. Relative retention volumes of chlorinated *o*-cresols. Length of column: 2 m. 100 ml He/min. Column packing Perkin Elmer A (20 % Di-decyl-phthalate on Chromosorb)

Compound	Relative retention volume (V_R for *o*-cresol = 1)	
	150°C	175°C
o-Cresol	1.00	1.00
6-Chloro-*o*-cresol	0.70	0.78
4-Chloro-*o*-cresol	5.46	4.65
4,6-Dichloro-*o*-cresol	2.52	2.48

Table 4. Analyses of chlorinated *o*-cresols.

Analysis number	Compound	% Found	% Known weight	Dev.	% Known mole	Dev.
1	*o*-Cresol	25.4	21.4	+4.0	27.6	−2.2
	6-Chloro-*o*-cresol	12.8	13.0	−0.2	12.8	±0
	4-Chloro-*o*-cresol	42.8	41.6	+1.2	40.8	+2.0
	4,6-Dichloro-*o*-cresol	19.0	24.0	−5.0	18.9	+0.1
2	*o*-Cresol	11.9	10.2	+1.7	13.5	−1.6
	6-Chloro-*o*-cresol	14.7	14.6	+0.1	14.6	+0.1
	4-Chloro-*o*-cresol	59.7	57.6	+2.1	57.7	+2.0
	4,6-Dichloro-*o*-cresol	13.8	17.6	−3.8	14.2	−0.4
3	*o*-Cresol	5.8	4.7	+1.1	6.2	−0.4
	6-Cloro-*o*-cresol	12.9	13.1	−0.2	13.2	−0.3
	4-Chloro-*o*-cresol	76.6	76.0	+0.6	75.6	+1.0
	4,6-Dichloro-*o*-cresol	4.8	6.3	−1.5	5.1	−0.3
4	*o*-Cresol	7.0	6.1	+0.9	8.1	−1.1
	6-Chloro-*o*-cresol	7.0	6.8	+0.2	6.8	+0.2
	4-Chloro-*o*-cresol	78.7	77.3	+1.4	77.3	+1.4
	4,6-Dichloro-*o*-cresol	7.3	9.8	−2.5	7.9	−0.6

Elution time at 175°C with column packing A was 60 min. Quite satisfactory separation of the four cresols was obtained. Another useful column packing has been recommended to me by Prawitz,[6] namely 4 g Apiezon and 6 g diglycol on 40 g Silocel C 22.

With column packing Perkin Elmer A and a temperature of 175°C a number of analyses on prepared samples with the four cresols in different concentrations were performed. The results are given in Table 4. The percentages of the four cresols have been calculated from the peak areas without the use of correction factors.

The agreement between known and found values are relatively good at least for 4 chloro-*o*-cresol and 6-chloro-*o*-cresol, which are the main constituents in the technical 4-chloro-*o*-cresol. For higher accuracy, correction factors for the peak areas must be determined. That can easily be done by the preparation and analysis of a suitable number of synthetic mixtures of known compositions.

Having achieved this simple gas cromatographic analysis for the chlorinated *o*-cresols it was found very desirable to try to determine chlorinated *o*-toloxyacetic acids by splitting them into the corresponding chlorinated *o*-cresols. The analysis of the chlorinated toloxyacetic acids has for a long time been an important and difficult problem.

The *o*-toloxyacetic acids cannot be hydrolyzed completely by heating with aqueous solutions of hydrogen halides. Using pyridine hydrochloride [7], however, a quantitative splitting of the chlorinated *o*-toloxyacetic acids to the

corresponding *o*-cresols could be achieved. For this reaction and for the analysis the following procedure was used.

0.5—1.0 g chlorinated *o*-toloxyacetic acid was refluxed with 3 g pyridine hydrochloride for 8 h at 210—220°C. After cooling, the reaction mixture was diluted with 10 ml water. No unreacted toloxyacetic acid could be found. The cresols were extracted with 2 × 2 ml isopropyl ether. The etherial solution was, without further treatment injected into the Gas Fractometer and analyzed. The peaks of the solvent and a small amount of pyridine were not accounted for. The results of the analyses of some prepared mixtures of chlorinated *o*-toloxyacetic acids according to this method are given in Table 5. Correction factors for the peak areas have not been used.

Experiments on a somewhat larger scale have also been made in which it was tried to recover the cresols as completely as possible. Yields of 97—98 % were obtained and the cresols were of high purity.

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Table 5. Analyses of chlorinated *o*-toloxyacetic acids.

Analysis number	Compound	% Found	% Known weight	Dev.
1	*o*-Toloxyacetic acid	32.1	32.8	−0.7
	6-Chloro-*o*-toloxyacetic acid	23.8	23.6	+0.2
	4-Chloro-*o*-toloxyacetic acid	21.7	20.6	+1.1
	4,6-Dichloro-*o*-toloxyacetic acid	22.4	23.0	−0.6
2	*o*-Toloxyacetic acid	13.3	13.9	−0.6
	6-Chloro-*o*-toloxyacetic acid	42.5	42.7	−0.2
	4-Chloro-*o*-toloxyacetic acid	26.7	25.2	+1.5
	4,6-Dichloro-*o*-toloxyacetic acid	17.5	18.3	−0.8
3	*o*-Toloxyacetic acid	18.2	17.8	+0.4
	6-Chloro-*o*-toloxyacetic acid	28.3	27.8	+0.5
	4-Chloro-*o*-toloxyacetic acid	42.3	42.3	±0
	4,6-Dichloro-*o*-toloxyacetic acid	11.2	12.2	−1.0
4	*o*-Toloxyacetic acid	10.4	10.7	−0.3
	6-Chloro-*o*-toloxyacetic acid	22.9	23.1	−0.2
	4-Chloro-*o*-toloxyacetic acid	52.3	50.9	+1.4
	4,6-Dichloro-*o*-toloxyacetic acid	14.4	15.3	−0.9
5	*o*-Toloxyacetic acid	4.0	4.1	−0.1
	6-Chloro-*o*-toloxyacetic acid	3.8	3.9	−0.1
	4-Chloro-*o*-toloxyacetic acid	88.3	87.7	+0.6
	4,6-Dichloro-*o*-toloxyacetic acid	3.9	4.4	−0.5

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