INDIRECT DETERMINATION OF CHLOROPHENOLS BY ATOMIC ABSORPTION SPECTROMETRY (AAS) AFTER EXTRACTION OF THEIR IONIC ASSOCIATES INVOLVING THE DIPYRIDYLOCOPPER(II) OR PHENANTHROLINOCOPPER(II) COMPLEX

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A novel method was developed for the indirect determination of chlorophenols by AAS after extraction of their ionic associates involving the dipyridylocopper(II) (CuDP) or phenanthrolinocopper(II) (CuPH) complex into nitrobenzene, *o*-dichlorobenzene or methyl isobutyl ketone. Nitrobenzene appeared to be particularly suitable for the extraction of the CuDP associate, methyl isobutyl ketone, for the extraction of the CuPH associate. The method is applicable to chlorophenol concentrations of 10^{-6} to 10^{-7} mol l^{-1}. Using CuDP after a single complete extraction into 10 ml of nitrobenzene, the lowest determinable concentration giving rise to absorbance $A = 0.010$ is 0·3 mg of pentachlorophenol in a litre; using CuPH after a single extraction into 10 ml of methyl isobutyl ketone, it is 0·2 mg of chlorophenol in a litre.

Chlorophenols are common products of chemical industry. They find application in agriculture as agents against dicotyledonous weeds, for the protection of wood against insects including termites, as well as in other fields of activity of man. They pass into soil, water and air, thereby stressing the environment[1].

Increased interest is being shown in new methods for the quantitation of chlorophenols. Converted to their acetyl derivatives, they were determined by gas chromatography[2] (also combined with mass spectrometry[3]), by thin layer chromatography[4], spectrophotometrically[5,6], as well as by liquid chromatography with chemiluminescence detection[7]. Yamamoto and coworkers[8] were able to demonstrate the feasibility of employing the associate of the phenanthrolinoiron(II) complex (FePH) with pentachlorophenol (PCP) extracted into nitrobenzene for the indirect determination of PCP by atomic absorption spectrometry (AAS).

In the present work we applied to the determination of chlorophenols a modification of the last-mentioned method, replacing the iron(II) complex with the dipyridylocopper(II) (CuDP) or phenantrolinocopper(II) (CuPH) complex. Examined wathe determination of pentachlorophenol, 2,4,5-trichlorophenol, and 2,4,6-trichloros phenol in model samples. The developed methods of indirect determination of chlorophenols were applied to pesticide agents used in agriculture.

EXPERIMENTAL

Chemicals and Apparatus

Pentachlorophenol (PCP) and 2,4,5-and 2,4,6-trichlorophenols (TCP) of pure grade were obtained from Koch–Light (U.K.) and additionally purified as follows. PCP was dissolved in distilled water and filtered. After making the filtrate acidic with hydrochloric acid, the precipitated PCP was filtered out and recrystallized twice from an aqueous–ethanolic (1 : 1 w/w) solution. The melting temperature of the needle-shaped crystals was 190–191°C. The trichlorophenols were dissolved in distilled water and filtered; crystallization from a cold aqueous–ethanolic solution afforded white crystals. The melting temperatures of 2,4,5-TCP and 2,4,6-TCP were 65–66°C (ref.[9]: 66–67°C) and 66–67°C (ref.[9]: 68°C), respectively.

Solutions of the chlorophenol were prepared so that the chosen amount of the solid, placed in a 100 ml volumetric flask, was dissolved in 20 ml of ethanol and diluted to the mark with distilled water. In the case of PCP, several drops of 0·2M-NaOH were added before dilution in order to prevent formation of precipitate.

The dipyridylocopper(II) and phenanthrolinocopper(II) complexes at a concentration of 10 mmol l^{-1} were prepared by dissolving 0·6242 g of copper(II) sulfate pentahydrate in a 250 ml volumetric flask and adding 1·1715 g of 2,2′-dipyridyl or 1·4867 g of 1,10-phenanthroline. After complete dissolution, which could take several days (dipyridyl), the flask contents were diluted to the mark.

The other chemicals used were products of Lachema, Brno; *o*-dichlorobenzene (DCB) was supplied by VEB Laborchemie Apolda. Suitable pH for the measurement was adjusted by means of Britton–Robinson buffers.

The atomic absorption measurements were performed on an 1N AAS instrument (Zeiss, Jena) using acetylene-air flame. Copper was determined at 324·7 nm. The pH was measured on an MV 870 Digital instrument of Präcitronic Dresden.

Procedures

The following procedure was adopted for examining the dependence of absorbance of the extracted associate at 324·7 nm on the aqueous solution acidity. In each of two sets of 25 ml volumetric flasks were placed 10 ml of the Britton–Robinson buffer at a chosen pH, 5 ml of chlorophenol solution at a concentration between 1·0 and 2·0 mol l^{-1}, and 5 ml of the dipyridylocopper(II) or phenanthrolinocopper(II) complex, and the system was diluted to the mark with distilled water. In the first set, the pH was measured. The mixed contents of the other set were transferred into 100 ml separating funnels. The volumetric flasks were rinsed twice with 5 ml of distilled water, which was then added to the separating funnel. A volume of 5 or 10 ml of the extracting agent was added, and extraction was conducted for two minutes. The organic phase was drawn off and 0·3 of anhydrous sodium sulfate was added to it. Subsequently, this phase was transferred into a ground-in test tube and fed directly into the AAS flame.

Calibration curves were obtained likewise. Chlorophenol stock solution was added in volumes of 0 to 5 ml. The calibration dependence $A = (a \pm s_a t_\alpha) + (b \pm s_b t_\alpha)c$ was evaluated by using the linear regression approach[10], a and b being the regression coefficients, s_a and s_b the standard deviations of coefficients a and b, respectively, and t_α the tabulated critical value for the chosen significance level (Table I). The correlation coefficient was never lower than 0·9990.

Determination of chlorophenols. A known amount (5–25 mg) of the chlorophenol in question was placed in a 100 ml volumetric flask, dissolved in 20 ml of ethanol, and made up to the mark with distilled water. For PCP, several drops of 0·2M-NaOH were added in order to facilitate its dissolution. Five replicate determinations were performed for each sample and subjected to

TABLE I

Characteristics of calibration regression straight lines in the determination of chlorophenols

Analyte	Complex	Extractant (ml)	n^a	c_s µmol l^{-1}	$a \pm s_a$	$b \pm s_b$ l mol^{-1}
PCP	CuDP	NB (10)	7	2·3 −23	−0·003 ± 0·003	0·883 ± 0·022
PCP	CuPH	NB (5)	5	5·96−35·8	−0·003 ± 0·007	0·828 ± 0·032
PCP	CuPH	MIBK (10)	8	1·45−17·5	0·004 ± 0·001	0·854 ± 0·015
2,4,6-TCP	CuDP	NB (5)	7	1·65−33·0	−0·004 ± 0·002	0·784 ± 0·008
2,4,6-TCP	CuDP	DCB (5)	6	2·19−43·9	−0·005 ± 0·001	0·538 ± 0·006
2,4,6-TCP	CuPH	MIBK (10)	5	5·31−31·8	0·001 ± 0·001	0·501 ± 0·005
2,4,5-TCP	CuDP	NB (10)	8	6·06−42·4	0·002 ± 0·002	0·385 ± 0·007

[a] Number of measurements.

TABLE II

Results of indirect determination of chlorophenols

Analyte	Complex	Extractant (ml)	Added mg l^{-1}	Found^a mg l^{-1}	ε^b %	s_r^c %
PCP	CuDP	NB (10)	0·50	0·54	8·20	2·93
			2·50	2·61	4·35	0·69
PCP	CuPH	NB (5)	0·52	0·51	−2·29	2·62
			2·00	1·98	−0·42	1·50
PCP	CuPH	MIBK (10)	0·55	0·54	−0·58	0·49
			2·13	2·24	5·24	0·52
2,4,6-TCP	CuDP	NB (5)	0·53	0·54	2·46	0·58
			2·01	1·99	−1·29	0·71
2,4,6-TCP	CuDP	DCB (5)	0·51	0·52	0·47	1·66
			2·01	2·03	1·29	0·25
2,4,6-TCP	CuPH	MIBK (10)	0·50	0·51	1·47	1·66
			2·11	2·12	0·53	0·70
2,4,5-TCP	CuDP	NB (10)	0·49	0·48	−2·06	0·63
			2·11	2·09	−0·53	0·61

[a] Average of five determinations; [b] relative error; [c] relative standard deviation.

statistical processing; the results are given in Table II. Solutions of pesticide agents analyzed for chlorophenols were prepared likewise, only the amount of the agent taken was as high as 50 mg.

RESULTS AND DISCUSSION

The underlying principle of the method of indirect determination of chlorophenols consists in the formation of an ionic associate with a defined composition which is readily extractable into a suitable solvent, applicable as an AAS medium. Using the continuous variations method, Yamamoto and coworkers[6] found that the phenanthrolinoiron(II) complex and PCP give an ionic associate of the composition $[Fe(phen)_3(C_6Cl_5O)_2]$. The copper(II) cation forms similar cationoid complexes with dipyridyl and with phenanthroline; the molar ratio is 1 : 3, stability constant $\log \beta = 17{\cdot}08$ and $21{\cdot}32$, respectively[11]. We assume that the CuDP and CuPH complexes are cations with two charges and that the ionic associates with chlorophenols are formed in the 1 : 2 ratio.

Nitrobenzene, *o*-dichlorobenzene and methyl isobutyl ketone (MIBK) were studied as the extracting solvents. For each of them, the minimal sufficient volume and/or the number of repeated extractions necessary for complete extraction of the associate were sought (Table III). With MIBK and DCB, single extraction was insufficient but no more than three extractions with small volumes of the solvent were necessary.

A suitable acidity of the aqueous phase is a prerequisite for the formation of the ionic associate and its complete extraction into the organic solvent. Extraction curves from which the optimum pH of the aqueous phase can be read were plotted for all the chlorophenols and copper complexes investigated (Fig. 1). The calibration curves for the determination of chlorophenols were constructed for the optimum pH values. The determination was performed with model solutions and applied to chlorophenol pesticides used in agricultural agents. The results of analyses of chlorophenols in model solutions are given in Table II, a survey of the suitability of using the complexes and extractants is shown in Table III. CuDP appears more suitable if the associates are extracted into nitrobenzene, whereas MIBK better suited to the extraction of associates involving the CuPH complex.

Yamamoto and coworkers employed FePH for the determination of PCP, extracting the associate into nitrobenzene. The calibration curve span reported by them is from 0 to $0{\cdot}3\ \text{mmol}\ l^{-1}$. A comparison with our results (Tables II and IV) demonstrates that CuDP and CuPH enable chlorophenols to be determined at lower concentrations. Moreover, we observed that an emulsion forms during the extraction of the associate comprising FePH; this emulsion is the richer the higher is the concentration of the chlorophenol to be determined. No such well-developed emulsion arises when using CuDP or CuPH; the slight haze that appears can be eliminated with a small amount of anhydrous sodium sulfate.

TABLE III

Sutability of the complexes and extractants studied for the determination of chlorophenols[a]

Analyte	CuDP			CuPH		
	NB	MIBK	DCB	NB	MIBK	DCB
PCP	++++	−	+	++++	+++	+
2,4,6-TCP	++++	+	+++	++	++++	+
2,4,5-TCP	++++	++++	+	+	−	+

[a] Necessary number of extractions: single into 5 ml (+++++) or into 10 ml (++++), double (++), triple (+).

TABLE IV

Characteristics of the indirect determination of chlorophenols using single extraction

Analyte	Complex	Extractant (ml)	Applicable pH range	c_s[a] μmol l^{-1}
PCP	CuDP	NB (10)	7·0—10·0	1·09
PCP	CuPH	NB (5)	5·5—11·0	1·19
PCP	CuPH	MIBK (5)	10·5—11·5	0·71
PCP	CuPH	MIBK (10)	10·5—11·5	0·71
2,4,6-TCP	CuDP	NB (5)	9·5—10·5	1·42
2,4,6-TCP	CuDP	DCB (5)	9·5—10·5	2·37
2,4,6-TCP	CuPH	MIBK (10)	10·5—11·0	2·02
2,4,5-TCP	CuDP	NB (10)	10·0—10·5	2·57

[a] Concentration causing absorbance $A = 0·010$.

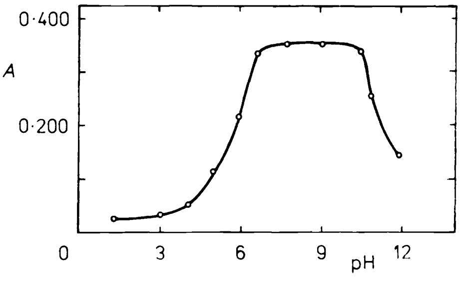

FIG. 1

Extraction curve of the associate of pentachlorophenol ($c = 0·116$ mmol l^{-1}) with the dipyridylocopper(II) complex into nitrobenzene ($V = 10$ ml)

PCP, 2,4,5-TCP and 2,4,6-TCP were quantitated in agricultural agents using the two complexes and the various extractants. All analyses were evaluated statistically and the differences in the standard deviations were subjected to the F-test[10] for $\alpha = 0{\cdot}05$. The values obtained were not statistically significant.

The determination can be influenced by some organic anions capable of forming extractable ionic associates with the complexes employed. These include, e.g., trichloroacetic acid or various higher-molecular-weight phenols such as 8-hydroxyquinoline and derivatives thereof[12]. On the other hand, alkylphenols and aminophenols do not interfere with the determination of chorophenols, as stated in ref.[13]

The accuracy of determination was assessed in terms of its relative error (Table II), the precision, in terms of the relative standard deviation. The lowest determinable concentration of PCP, using CuDP and applying extraction of the ionic associate into 10 ml of nitrobenzene, is 0·3 mg in a litre (after subtraction of the blank value). When using CuPH and extracting the associate into 10 ml of MIBK, the lowest determinable concentration of PCP is 0·2 mg in a litre.

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