

DETERMINATION OF SOME NITROPHENOLS BY ATOMIC ABSORPTION SPECTROMETRY (AAS) AFTER EXTRACTION OF IONIC ASSOCIATES INVOLVING THE BIPYRIDYLCOPPER(II) OR PHENANTHROLINOCOPPER(II) COMPLEX

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A new method has been developed for the indirect determination of nitroso- and nitrophenols by atomic absorption spectrometry (AAS) after extraction of ionic associates involving bipyridylcopper(II) (CuDP) or phenanthrolinecopper(II) (CuPH) complexes. Nitrobenzene and methyl isobutyl ketone appeared to be suitable for the extraction. It was possible to determine several tenths to hundredths of a milligram of nitrophenol in a litre. Extractable associates with CuDP and CuPH are formed by phenols possessing two substituents or by higher molecular weight phenols such as naphthol or hydroxyquinoline. Monosubstituted phenols fail to form associates of this kind.

Many nitrophenols which find applications in the chemical industry are also used in agriculture, mainly as herbicides, fungicides and insecticides. Very often, such substances are toxic and if applied wrongly, can have adverse impacts on the environment. New methods for the determination of nitrophenols have been developed recently. Liquid chromatography^{1,2} and gas chromatography^{3,4} have been used conventionally. Yamamoto et al.⁵ pointed to the feasibility of employing associate of the phenanthroline-iron(II) complex with pentachlorophenol after extraction into nitrobenzene for its indirect determination by AAS. In our previous work⁶ we demonstrated the possibility of quantitating chlorophenols by employing their associates with the CuDP and CuPH complex followed by extraction into various solvents as a means of indirect determination by AAS. In the present work we examined the feasibility of determining nitroso- and nitrophenols after extraction of ionic associates involving the CuDP and CuPH complexes.

EXPERIMENTAL

Chemical and Apparatus

The atomic absorption measurements were performed on an 1 N AAS instrument (Zeiss, Jena) using acetylene-air flame and gas from pressure bottles. The determination of copper was carried out at 327.7 nm. The pH values were measured with a Pracitronic (Dresden) pH meter.

The formation of ionic associates and their use in the determination of compounds after extraction into organic solvents were studied for the following substances: phenol, 2-nitrophenol (*I*), 3-nitrophenol (*II*), 4-nitrophenol (*III*), 3-aminophenol (*IV*), 4-aminophenol (*V*), 2,4-dinitrophenol (*VI*), 2-amino-4-nitrophenol (*VII*), 2,4,6-trinitrophenol (*VIII*), 2,4-dinitro-6-methylphenol (*IX*), 2-(2-butyl)-4,6-dinitrophenol (*X*), 2-nitro-1-naphthol (*XI*), 1-nitroso-2-naphthol (*XII*). Compound *IX* was isolated from the technical product Nitrosan (Chemopetrol, Spolana Neratovice), compound *X* was isolated from the technical product Ladob (Lachema, Brno).

The purity of the substances isolated from the technical products was tested by elemental analysis using a Perkin-Elmer Elemental Analyser 240 and by melting point measurement⁷, the other phenols were reagent grade products of Lachema, Brno. The purity of all substances was checked by melting point measurements using a Kofler apparatus.

Stock solutions of the phenols were prepared by dissolving the substances in 5 to 10 ml of ethanol and diluting the system with water to mark in a 100 ml volumetric flask. In cases where the dissolution was incomplete, several drops of 0.2 M NaOH were added before dilution to the mark.

The dipyrildylcopper(II) (CuDP) and phenanthrolinecopper(II) (CuPH) 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-bipyridyl or 1.4867 g of 1,10-phenanthroline. After complete dissolution, which took several days in some cases (bipyridyl), the flask contents were diluted to the mark with water.

Nitrobenzene (NB) was a product of Lachema, Brno, *o*-dichlorobenzene (DCB) was supplied by Laborchemie Apolda, and methyl isobutyl ketone (MIBK) was obtained from Ubichem, England.

The pH values of the solutions were adjusted by using Britton-Robinson buffers, without ionic strength adjustment of the solution⁸.

Procedures

The absorbance of the extracted associate at 324.7 nm depends on the acidity of the solution. In each of two sets, 5 ml of nitrophenol at a concentration between $5.0 \cdot 10^{-5}$ – $1.0 \cdot 10^{-4}$ mol l⁻¹, 5 ml of CuDP or CuPH, and 10 ml of Britton-Robinson solution at the appropriate pH were added to a 25 ml volumetric flask and diluted to the mark with distilled water. The pH of the first set was measured, whereas the mixed contents of the other set were transferred to a 100 ml separating funnel and the appropriate volume of the organic solvent was added. The extraction was conducted for 2 min and the organic phase was drawn off and dried with 0.3 g of anhydrous sulfate. This phase was transferred to a stoppered tube and fed directly into the AAS flame. Extraction curves were obtained as absorbance versus pH plots (Fig. 1), which gave the optimum pH for the calibration curves and determination of phenol.

Calibration straight lines were obtained in a similar way. Volumes of 0 to 2 ml of nitrophenol, 10 ml of Britton-Robinson buffer of a suitable pH, and 5 ml of the CuDP or CuPH complex were added to a 25 ml volumetric flask, diluted to the mark, and extracted with the organic solvent of choice. The organic phase was drawn off and its absorbance was measured.

The calibration dependence $y = (a - s_a t_\alpha) + (b - s_b t_\alpha) c$, where a , b are regression coefficients and t_α is the tabulated critical value for the significance level chosen (Table I), was evaluated by linear regression⁹. The correlation coefficients r were never lower than 0.9985.

Determination of nitrophenols. In a 100 ml volumetric vessel was placed 2 to 15 mg of nitrophenol and dissolved in 5 to 10 ml of ethanol before making up to the mark with distilled water. Five determinations were performed for each sample and the results, which are given in Table II, were statistically processed.

RESULTS AND DISCUSSION

The indirect determination of nitrophenols by the above method is based on the formation of an ionic associate of nitrophenol with CuPH or CuDP possessing a defined composition, which can be extracted into an organic solvent. Using the continuous variations method, Yamamoto¹⁰ found that the composition of the associate of FePH with pentachlorophenol (PCP) is $[\text{Fe}(\text{PH})_2(\text{PCP})_2]$. The copper(II) cation forms similar cationoid complexes with dipyridyl and with phenanthroline. The molar ratio is 1 : 3, the stability constants are $\log \beta = 17.08$ and 21.32, respectively¹¹. We suggest that the CuDP and CuPH complexes are cations with two charges and that the ionic associates with nitrophenols are formed in the 1 : 2 molar ratio.

Nitrobenzene, *o*-dichlorobenzene and methyl isobutyl ketone were tested as the extracting solvents. For each of them, the minimal sufficient volume and the number of repeated extractions necessary for a complete extraction of the associate were established. Nitrobenzene and methyl isobutyl ketone appeared to be suitable, and a single extraction with 5 or 10 ml of solvent proved to be sufficient. Nitrobenzene was found to suit well in the majority of applications. The detection limit for the determination of nitrophenols was lower when using methyl isobutyl ketone. *o*-Dichlorobenzene could be used in some cases only and a single extraction was insufficient. The process was unsuitable if the extract from the sample had to be extracted more than twice. The parameters characterizing the indirect determination of chlorophenols using a single extraction are given in Table III.

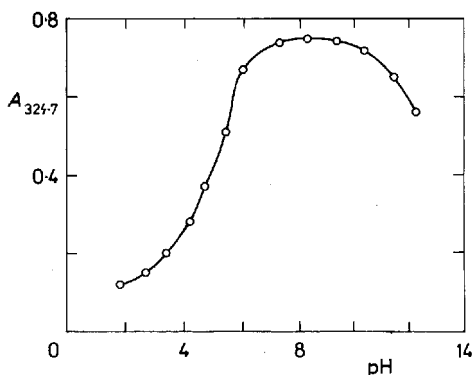


FIG. 1

Extraction curve of the associate of 2,4-dinitrophenol ($c = 1.06 \cdot 10^{-6} \text{ mol l}^{-1}$) with the phenanthroline-copper(II) complex into nitrobenzene ($V = 5 \text{ ml}$)

TABLE I
Parameters of calibration regression straight lines in the determination of nitrophenols

Analyte	Complex	Extractant (ml)	n^a	c_s $\mu\text{mol l}^{-1}$	$a \pm s_a$	$b \pm s_b$ l mol^{-1}
VI	CuDP	NB (5)	7	2.05 – 20.93	-0.002 ± 0.001	0.751 ± 0.022
	CuPH	NB (5)	7	2.20 – 21.35	0.001 ± 0.002	0.597 ± 0.020
	CuDP	MIBK (10)	7	2.25 – 20.05	-0.003 ± 0.003	0.529 ± 0.016
VII	CuPH	NB (2 × 5)	7	1.65 – 20.83	0.003 ± 0.002	0.478 ± 0.009
	CuDP	NB (10)	7	3.50 – 20.05	-0.004 ± 0.003	0.519 ± 0.014
VIII	CuDP	NB (10)	7	4.56 – 10.78	-0.007 ± 0.007	0.386 ± 0.015
	CuPH	DCB (2 × 5)	7	4.21 – 18.22	0.004 ± 0.002	0.453 ± 0.012
IX	CuDP	MIBK (5)	7	1.02 – 17.02	0.004 ± 0.004	0.905 ± 0.031
	CuPH	MIBK (10)	7	0.80 – 15.22	0.005 ± 0.004	0.889 ± 0.026
	CuDP	NB (10)	7	1.69 – 22.45	0.003 ± 0.002	0.234 ± 0.006
	CuPH	NB (10)	7	1.60 – 26.35	0.004 ± 0.003	0.239 ± 0.008
	CuDP	DCB (2 × 5)	7	3.53 – 31.83	-0.004 ± 0.003	0.231 ± 0.007
	CuDP	MIBK (10)	7	1.65 – 25.30	-0.002 ± 0.004	0.473 ± 0.011
	CuPH	MIBK (10)	7	1.50 – 21.05	-0.001 ± 0.002	0.733 ± 0.008
	CuDP	NB (5)	7	3.50 – 20.35	0.002 ± 0.002	0.280 ± 0.008
	CuPH	NB (5)	7	2.60 – 21.20	0.004 ± 0.003	0.377 ± 0.011
	CuDP	MIBK (5)	7	3.67 – 18.34	0.005 ± 0.004	0.783 ± 0.025
X	CuPH	MIBK (5)	7	3.67 – 18.34	0.004 ± 0.002	0.511 ± 0.012
	CuDP	NB (5)	7	2.50 – 25.00	0.001 ± 0.002	0.534 ± 0.016
XI	CuPH	NB (5)	7	2.70 – 18.52	0.005 ± 0.003	0.675 ± 0.018
	CuDP	NB (5)	7	1.95 – 25.20	0.002 ± 0.001	0.763 ± 0.013
XII	CuPH	NB (5)	7	2.35 – 23.50	-0.006 ± 0.003	0.705 ± 0.017
	CuDP	DCB (5)	7	2.35 – 25.20	-0.003 ± 0.003	0.794 ± 0.019
	CuPH	DCB (5)	7	1.95 – 19.20	-0.004 ± 0.002	0.813 ± 0.018
	CuDP	MIBK (5)	7	1.95 – 20.15	-0.006 ± 0.005	0.856 ± 0.034
	CuPH	MIBK (5)	7	1.90 – 19.75	-0.004 ± 0.003	0.799 ± 0.020

^a Number of measurements.

TABLE II
Results of indirect determination of nitrophenols

Analyte	Complex	Extractant (ml)	Added mg l ⁻¹	Found ^a mg l ⁻¹	Δy^b , %	s_r^c %
<i>VI</i>	CuDP	NB (5)	0.50	0.51	2.00	1.61
			0.94	0.93	-1.06	1.20
	CuPH	NB (5)	0.48	0.47	-2.08	2.68
			0.95	0.94	-1.05	1.05
	CuDP	MIBK (10)	0.52	0.53	1.92	2.63
			0.94	0.93	-1.06	2.00
<i>VII</i>	CuPH	NB (2 × 5)	0.26	0.27	3.85	3.21
			0.80	0.79	-1.25	2.70
<i>VIII</i>	CuDP	NB (10)	0.32	0.30	-6.25	4.26
			1.00	0.97	-3.00	2.16
	CuPH	NB (10)	0.50	0.48	-4.00	4.41
			1.00	0.96	-4.00	3.06
	CuPH	PCB (5)	0.38	0.39	2.63	2.97
			1.00	0.99	-1.09	1.09
	CuDP	MIBK (5)	0.30	0.31	3.33	3.51
			0.95	0.93	-2.11	2.56
	CuPH	MIBK (10)	0.17	0.16	-5.88	1.74
			0.75	0.76	1.33	1.02
<i>IX</i>	CuDP	NB (10)	0.60	0.59	-1.67	3.01
			1.20	1.19	-0.83	2.84
	CuPH	NB (10)	0.50	0.51	2.00	2.97
			1.00	0.99	-1.00	1.69
	CuDP	DCB (2 × 5)	0.68	0.69	1.47	3.04
			1.25	1.23	1.60	1.41
	CuDP	MIBK (10)	0.50	0.49	-2.00	1.89
			1.08	1.07	0.92	1.32
	CuPH	MIBK (10)	0.40	0.41	2.50	1.84
			1.10	1.09	-0.91	1.52
Nitrosan, <i>IX</i> (Technical product)	CuDP	NB (10)	0.72	0.79	10.56	6.7
	CuPH	NB (10)	0.72	0.78	8.39	5.6
	CuDP	MIBK (10)	0.72	0.78	7.63	5.6
	CuPH	MIBK (10)	0.72	0.77	7.01	3.6

TABLE II
(Continued)

Analyte	Complex	Extractant (ml)	Added mg l ⁻¹	Found ^a mg l ⁻¹	Δy^b , %	s_r^c %
X	CuDP	NB (5)	0.81	0.82	1.23	3.00
			1.07	1.06	0.93	2.75
	CuPH	NB (5)	0.56	0.45	-2.17	2.93
			0.96	0.95	-1.04	2.72
	CuDP	MIBK	0.49	0.48	-2.04	2.53
			1.00	0.99	-1.00	0.91
	CuPH	MIBK	0.65	0.64	-1.54	2.98
			1.10	1.11	0.91	2.66
XI	CuDP	NB (5)	0.39	0.38	-2.56	2.81
			8.84	0.83	-1.19	1.98
	CuPH	NB (5)	0.45	0.46	2.22	3.03
			0.85	0.86	1.18	1.76
XII	CuDP	NB (5)	0.35	0.36	0.29	2.61
			0.78	0.80	2.26	1.56
	CuPH	NB (5)	0.36	0.35	-2.78	3.02
			0.78	0.79	1.28	1.78
	CuDP	DCB (5)	0.38	0.37	-2.63	2.99
			0.77	0.76	-1.29	1.22
	CuPH	DCB (5)	0.39	0.40	2.56	3.16
			0.74	0.75	1.35	1.71
CuDP	MIBK (5)	0.28	0.27	-3.57	2.01	
		0.80	0.79	-1.25	2.02	
CuPH	MIBK (5)	0.41	0.42	2.44	3.96	
		0.80	0.81	1.25	3.51	

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

The method proved to be suitable for the determination of 2-amino-4-nitrophenol, 2,4-dinitro-6-methylphenol, 2-nitro-1-naphthol, 1-nitroso-2-naphthol, 2,4,6-trinitrophenol-2,4-dinitro-6-methylphenol and 2-butyl-4,6-dinitrophenol (Table II). Good results were achieved particularly in the determination of higher molecular weight substances such as 1-nitroso-2-naphthol and picric acid, containing three nitro groups with a strong negative M-effect.

TABLE III
Characteristic of the indirect determination of nitrophenols using single extraction

Analyte	Complex	Extractant	Applicable pH range	c_s^a mg l ⁻¹
VI	CuDP	NB (5)	7.00 – 10.50	0.375
	CuPH	NB (5)	7.00 – 10.00	0.350
	CuDP	MIBK (10)	10.50 – 12.10	0.390
VII	CuPH	NB (2 × 5)	8.90 – 12.10	0.180
VIII	CuDP	NB (10)	6.00 – 8.50	0.310
	CuPH	NB (10)	6.00 – 10.00	0.455
	CuPH	DCB (2 × 5)	9.00 – 11.00	0.385
	CuDP	MIBK (5)	5.00 – 7.50	0.120
	CuPH	MIBK (10)	6.50 – 12.00	0.085
IX	CuDP	NB (10)	7.70 – 9.20	0.245
	CuPH	NB (10)	8.00 – 11.50	0.205
	CuDP	DCB (2 × 5)	7.30 – 8.90	0.300
	CuDP	MIBK (10)	8.90 – 10.50	0.250
	CuPH	MIBK (10)	7.90 – 10.20	0.200
X	CuDP	NB (5)	9.00 – 10.50	0.650
	CuPH	NB (5)	8.80 – 12.00	0.455
	CuDP	MIBK (5)	7.30 – 12.00	0.310
	CuPH	MIBK (5)	8.00 – 11.50	0.470
XI	CuDP	NB (5)	7.70 – 10.60	0.320
	CuPH	NB (5)	7.30 – 10.00	0.385
XII	CuDP	NB (5)	7.00 – 11.50	0.240
	CuPH	NB (5)	7.00 – 10.50	0.270
	CuDP	DCB (5)	7.30 – 10.50	0.265
	CuPH	DCB (5)	8.90 – 12.00	0.235
	CuDP	MIBK (5)	11.00 – 12.00	0.195
	CuPH	MIBK (5)	10.50 – 12.00	0.185

^a Concentration causing absorbance $A = 0.010$.

The determination was performed using model samples. The method was also tested for the determination of 2,4-dinitro-6-methylphenol in the technical product Nitrosane, whose aqueous solution is used for spraying trees against pests in spring. The F test⁹ revealed that variations of the results lie within the limits of random errors.

The accuracy of the results was evaluated in terms of the relative error, which was within the range of 5%. The precision was assessed in terms of the relative standard deviation, which lay within the range of 4%.

The method appeared to be most sensitive for the determination of 2,4,6-trinitrophenol after the formation of the ionic associate with CuPH, followed by extraction into 10 ml of MIBK. A concentration of 0.085 mg l^{-1} could be determined in this case. Using the CuDP complex and extraction into 5 ml of MIBK, 0.12 mg of 2,4,6-trinitrophenol in a litre could be quantitated.

The method is inapplicable to the determination of phenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 3-aminophenol and 4-aminophenol, since these compounds fail to form ionic associates with the CuPH and CuDP complexes, presumably because their molecules are not bulky enough. The result of this study of the formation of associates of the CuDP and CuPH complexes with nitrophenol, taking into account our previous results and those obtained by Koch, Ackermann and Lindner¹², give evidence that the number of substituents on the phenol plays a major role in the formation of the ionic associate. Associates with the CuDP or CuPH complexes are formed by phenols with two substituents or by some higher-molecular-weight phenols such as naphthol and hydroxyquinoline. The more substituents of the phenol base, the better formation of ionic associates. Monosubstituted phenols fail to form such ionic associates.

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