

# Determination of Some Organic Chloro Acids by Atomic Absorption Spectrometry (AAS) after Extraction of Their Ion-Associates with the Dipyridylcopper(II) or Phenanthrolinecopper(II) Complex

V. STUŽKA and Z. ŠEVČÍKOVÁ

*Department of Analytical and Organic Chemistry, Faculty of Natural Sciences, Palacký University, CZ-771 46 Olomouc*

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A new method for the determination of aliphatic chloro acids by atomic absorption spectrometry after the extraction of their ion-associates involving dipyridylcopper(II) and phenanthrolinecopper(II) complexes was elaborated. Nitrobenzene was used as a suitable extraction solvent. The method enabled to determine units of a milligram of trichloroacetic acid and 2,2'-dichloropropionic acid in pesticide preparations.

It has been known that due to a substitution of a lower fatty acid by chlorine the biological activity of herbicides arises while chloro derivatization in another position decreases the mentioned activity. The substitution of this chlorine by another halogen and the extension of the aliphatic chain leads to the efficiency decrease [1].

The most efficient representatives of this series of pesticides are trichloroacetic acid (TCA) and sodium salt of 2,2'-dichloropropionic acid (DCPA), marked DALAPON, contained in the herbicide preparation SYS 67 OMNIDEL. Both substances precipitate the proteins. For this reason they exhibit toxic effects for all plant enzymes.

A number of cations of bivalent metals generate with 2,2'-dipyridyl and 1,10-phenanthroline stable cationoid complexes [2]. The Cu(II) cation forms the 2,2'-dipyridyl and 1,10-phenanthroline cationoid complexes in the mole ratio 1:3, the stability constants of which are expressed by  $\log \beta = 17.08$  resp. 21.35 [3]. With bulky anions, these complexes form ion-associates extractable into organic solvents. It is assumed that the bivalent complexes form with monovalent anions of chloro acids associates in the mole ratio 1:2. The similar associates are formed even with chlorophenols and nitrophenols [4, 5].

We have been trying to find new methods for the determination of various anions of organic compounds. Herein, a new method of determination of aliphatic chloro acids is suggested. The determination is based on the formation of ion-associates of anions of chlorine organic acids with cationoid dipyridylcopper(II) (CuDP) or phenanthrolinecopper(II) (CuPH) com-

plexes which may be extracted to an organic solvent suitable for the introduction of air-acetylene flame of the atomic absorption spectrometer. In our previous works chlorophenols [4] and nitrophenols [5] were determined.

## EXPERIMENTAL

Monochloroacetic acid (MCA) (anal. grade, Avodante), methyl isobutyl ketone (Ubichem), and *o*-dichlorobenzene (Apolda) were used as supplied. The other chemicals used for the preparation of solutions were products of Lachema and were of anal. grade. 2,2'-Dichloropropionic acid (DCPA) was isolated as sodium salt from the technical preparation SYS 67 OMNIDEL (Lachema), containing 85 % of DALAPON, as follows: 5–7 g of the preparation was dissolved in 100 cm<sup>3</sup> of the distilled water. The filtrate was evaporated by infra-radiator in a porcelain dish to dryness. The yellow substance was recrystallized from 50 cm<sup>3</sup> of ethanol, filtered, and washed with diethyl ether. The dry, lustrous-white substance gave satisfactory elemental analysis (Perkin—Elmer).

The exact concentration of solutions of chloro acids used was determined by the titration with the solution of sodium hydroxide to phenolphthalein. Preparation of the dipyridylcopper(II) (CuDP) and phenanthrolinecopper(II) (CuPH) complexes and a similar iron(II) complex with the concentration 0.01 mol dm<sup>-3</sup> has been described in [4].

For the measurements of atomic absorption, the apparatus AAS 1 N (Zeiss) was used. The copper determination was realized at the wavelength 324.7

Table 1. Characteristic of Calibration Regression Straight Lines in the Determination of Chloro Acids

Compound	Complex	Extractant (V/cm <sup>3</sup> )	m <sup>a</sup>	$\frac{c_s}{\mu\text{mol dm}^{-3}}$	$\frac{a \pm s_a t_\alpha}{\text{dm}^3 \text{ mol}^{-1}}$	$\frac{b \pm s_b t_\alpha}{\text{dm}^3 \text{ mol}^{-1}}$
MCA	CuDP	NB (10)	35	100—500	-0.0034 ± 0.0031	0.9858 ± 0.0073
TCA	CuDP	NB (10)	25	10—50	0.0057 ± 0.0044	0.5721 ± 0.0095
DCPA	CuDP	NB (5)	30	40—500	-0.0055 ± 0.0069	0.2951 ± 0.0379
DCPA	CuPH	NB (5)	40	40—200	-0.0015 ± 0.0031	0.6854 ± 0.0176

a) Number of all measurements used for calibration curve,  $t_\alpha$  – Student's criterion.

Table 2. Results of Determination of Chloro Acids

Analyte	Complex	Extractant (V/cm <sup>-3</sup> )	$\rho(\text{Added})$ mg dm <sup>-3</sup>	$\rho(\text{Found})^a$ mg dm <sup>-3</sup>	$\frac{e_r^b}{\%}$	$\frac{s_r^c}{\%}$
MCA	CuDP	NB (5)	0.894	0.892	-0.22	1.04
			2.002	1.970	-1.60	0.57
MCA	CuDP	NB (10)	0.804	0.811	0.87	1.16
			2.109	2.120	0.52	0.69
TCA	CuDP	NB (5)	1.502	1.485	-1.13	1.17
			2.407	2.417	-0.42	0.48
TCA	CuDP	NB (10)	1.441	1.525	2.27	1.08
			2.502	2.610	4.32	0.78
DCPA	CuPH	NB (5)	0.520	0.506	-2.69	1.57
			2.104	2.094	-0.48	0.57
DCPA	CuDP	NB (5)	1.501	1.450	-2.73	0.52
			2.505	2.528	0.92	0.62
SYS1	CuDP	NB (5)	3.000	2.221	25.97	0.92
SYS1	CuPH	NB (5)	3.000	2.243	25.24	0.80
SYS2	CuDP	NB (5)	3.000	2.314	22.87	0.98
SYS2	CuPH	NB (5)	3.000	2.296	23.47	0.87

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

nm using the air-acetylene flame and the gasses were supplied from pressure bottles. The pH measurements were carried out using a Pracitronic apparatus.

The absorbance measurement of an ion-associate extract depends considerably on pH of the solution. The suitable pH of the extraction was obtained as follows. Two sets of 25 cm<sup>3</sup> volumetric flasks were filled with 5 cm<sup>3</sup> of a chloro acid solution, 5 cm<sup>3</sup> of CuDP or CuPH solution, and 10 cm<sup>3</sup> of Britton—Robinson solution with a distinct pH, and the volumetric flasks were adjusted with redistilled water. The first set of solutions was used for pH measurement. The mixed content of flasks of the second set was transferred into the 100 cm<sup>3</sup> separatory flasks and a selected amount of an organic solvent was added. After 2 min extraction and separation of the organic phase, 0.3 g of anhydrous sodium sulfate were added. The dried extract was transferred to a glass stoppered test tube and to the AAS flame. The extraction curves were obtained from the pH measurements and absorbance values (Fig. 1). The optimal pH for calibration curves (Table 1) was deduced from the shape of the extraction curves. The extractable associate was obtained from the horizontal sections of the extraction curves.

The calibration curves were obtained by a similar way. 25 cm<sup>3</sup> volumetric flasks were filled with 0—10

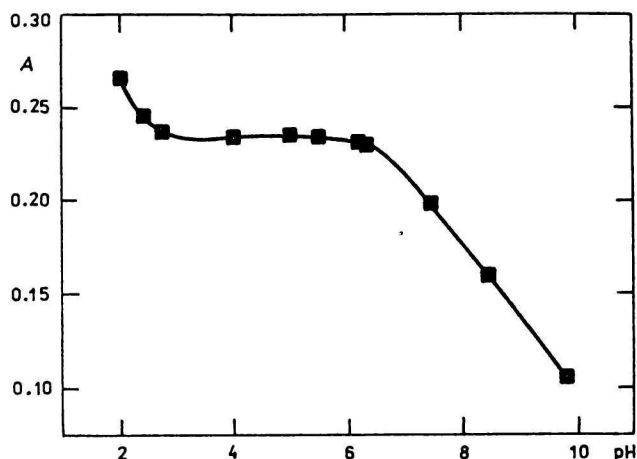


Fig. 1. Extraction of the associate of trichloroacetic acid ( $c = 4.2 \times 10^{-1}$  mol dm<sup>-3</sup>) with the dipirydicopper(II) complex into nitrobenzene ( $V = 10$  cm<sup>3</sup>).

cm<sup>3</sup> of the chloro acid solution, 10 cm<sup>3</sup> of Britton—Robinson buffer with a suitable pH and 5 cm<sup>3</sup> of the CuDP or CuPH complex. The volume was adjusted to 25 cm<sup>3</sup> and extracted with an organic solvent.

The calibration dependence

$$y = a + bx$$

was evaluated by the linear regression [6] using a computer.  $a, b$  are regression coefficients. The symbol  $x$  represents the concentration of chloro acid (mass or amount of substance concentration) and  $y$  is the absorbance for the concentration  $x$ . Intervals of confidence were calculated at individual calibration curves for coefficients  $a, b$  as given in Table 1. The accuracy of regression coefficients  $a, b$  was tested by the Student test [6]. The significance test of correlation coefficients was performed by comparison with critical values of correlation coefficients [6]. The characteristics of calibration curves are summarized in Table 2. The correlation coefficients were not lower than 0.9965.

### Chloro Acids Determination

The amount of 10 to 200 mg of a substance or a sample containing a chloro acid was placed in a 100 cm<sup>3</sup> volumetric flask and dissolved in water. Five parallel determinations of each sample were carried out, the results were statistically evaluated and are summarized in Table 3.

**Table 3.** Characteristic of the Indirect Determination of Chloro Acids Using Single Extraction

Analyte	Complex	Applicable pH range	$\frac{c^a}{\mu\text{mol dm}^{-3}}$
MCA	CuDP	3.8—5.5	658
TCA	CuDP	3.5—6.5	187
DCPA	CuPh	9.7—10.5	127
DCPA	CuDP	9.3—9.7	219

a) Concentration causing absorbance  $A = 0.010$ .

## RESULTS AND DISCUSSION

Nitrobenzene (NB), *o*-dichlorobenzene, and methyl isobutyl ketone were studied as extraction solvents. For the associate extraction, a minimal volume of the solvent was determined. The most suitable extraction solvent appeared to be nitrobenzene where a complete extraction was achieved only by one extraction with 5 cm<sup>3</sup> or 10 cm<sup>3</sup> of nitrobenzene. This solvent made possible to perform MCA and TCA determinations. Nitrobenzene appeared to be suitable also for DCPA determination using Cu(II) complexes. For the complete extraction using methyl isobutyl ketone, it was necessary to perform three up to four extractions. In case of *o*-dichlorobenzene, the associate was not completely extracted.

Fe(II) complexes did not appear to be convenient. In this case, ion-associates with chloro acids were

formed but, during the extraction, an emulsion was formed which was difficult to remove.

Under optimal conditions it was possible to determine 6.21 mg dm<sup>-3</sup> of MCA or 3.05 mg dm<sup>-3</sup> of TCA using CuDP complex and 10 cm<sup>3</sup> of nitrobenzene as the extraction agent. In the determination of DCPA using CuPH complex and 5 cm<sup>3</sup> of nitrobenzene, it was possible to determine 2.10 mg dm<sup>-3</sup>, with the CuDP complex it was 3.61 mg dm<sup>-3</sup> of DCPA. All determinations were statistically evaluated. The exactness of the determination was evaluated by the relative error which did not exceed 4.32 %. The precision of the determination was evaluated by the relative standard deviation not surpassing the value of 4.10 %. Suitable pH ranges for the determination of the substances studied and the lowest concentration of the determination are presented in Table 3.

DCPA was determined in two various products of pesticide preparations SYS 67 OMNIDEL using both complexes and nitrobenzene as the extraction agent. All the determinations were statistically evaluated and the difference of standard deviations was evaluated by *T*-test [6]. The calculated values for SYS1 and SYS2,  $F(5;5) = 1.1922$  resp. 1.2642 for  $d = 0.05$  are lower than the tabulated value 6.39. The exactness of the determination during analyses by both complexes is the same.

Both acidity and presence of substances forming with cationoid complexes ion-associates considerably influence the determination of chloro acids studied. As to inorganic anions, we can mention especially iodides, chlorides, sulfocyanates, perchlorates, chlorates, and bromides. As to organic substances, phenols with a higher molecular mass, chlorophenols, nitrophenols, and other more bulky organic anions should be mentioned. The reaction is not disturbed by sulfates, nitrates, and alkyl- and aminophenols.

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