

## STUDY OF SOME PROPERTIES OF DITHIOCARBAMATES DERIVED FROM HETEROCYCLIC AMINES

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Some physicochemical properties of sodium pentamethylenedithiocarbamate and complexes with Cu(II), Ni(II), and Fe(III) were studied. The bands in the electronic and IR absorption spectra were measured and characterized, and the possibility of coulometric determination of  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2\text{H}_2\text{O}$  was examined. The conditions for spectrophotometric determination of trace quantities of Cu(II), Ni(II), and Fe(III) as dithiocarbamate complexes were established and the stability constants of the complexes were determined.

Dithiocarbamic acids and their derivatives stemming from tetramethyleneimine, pentamethyleneimine, hexamethyleneimine, and tetramethylenediimine react with a number of metals with the formation of chelate-type complex compounds. These substances are more stable in solutions than other dithiocarbamates, therefore, they are employed as analytical reagents<sup>1,2</sup>.

The present work was devoted to the preparation and analytical application of some other physicochemical properties of sodium pentamethylenedithiocarbamate and its complexes with Cu(II), Ni(II), Fe(II), and Fe(III).

The preparation of the substances and some of their chemical properties as well as the application of  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2\text{H}_2\text{O}$  as precipitating agent have been reported<sup>3,4</sup>. The stability of the  $\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  complex in aqueous-ethanolic solutions has been studied by Janssen<sup>5</sup>, the stability of the  $\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  complex in dimethylformamide solutions was investigated by Toropova and co-workers<sup>6</sup>. The magnetic properties and electronic and infrared spectra of the copper, nickel, and ferric complexes have been given in ref.<sup>7</sup>, the crystal structure has been studied in refs<sup>8-10</sup>.

### EXPERIMENTAL

#### Apparatus

The electronic absorption spectra in the UV and visible region were scanned on a recording spectrophotometer Specord UV-VIS (Zeiss, Jena) using 1 cm cells. The infrared spectra were run in the region of 200—1600  $\text{cm}^{-1}$  on a spectrophotometer Perkin-Elmer 225 applying the

Nujol mull technique. The pH values of the buffers were measured on a Precision pH meter OP-205 with an electrode OP-711-LT/A (Radelkis, Budapest) against s.c.e. Coulometric titrations of  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  were accomplished on a coulometric analyzer OH-404 (Radelkis, Budapest).

#### Preparation of Dithiocarbamates

Crystalline preparation of  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  was obtained by applying the modified procedure<sup>3</sup>. The metal complexes were prepared by mixing equimolar volumes of 0.1M aqueous solutions of the metal sulfates and  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  and double or triple recrystallization from chloroform. The purity and composition of the substances prepared were examined by elemental analysis (Table I), determination of the melting or decomposition temperatures, gravimetrically, and in some instances also by coulometric analysis.

$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  can only be prepared in the presence of a strong reductant, otherwise the product is readily oxidized by atmospheric oxygen to the ferric complex. To obtain the substance  $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2\text{Cl}$ , the precipitate of the ferrous complex had to be dissolved in chloroform immediately after filtering out and washing with water; then it was allowed to crystallize. If the precipitate was dried before the dissolution in chloroform,  $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$  crystals resulted.

#### Working Procedure and Chemicals

Fresh solutions of dithiocarbamates for the spectrophotometric study were prepared by pipetting appropriate volumes of aqueous solution of  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  and solution of sulfate of the metal concerned into the solvent used. As the solvents were used glacial acetic acid, dimethylformamide, or ethanol-chloroform mixture 6 : 1, pipetted into 25 ml volumetric flasks in volumes of 20 ml (acetic acid), 22.5 ml (dimethylformamide) or 17.5 ml (mixed solvent) and diluted to volume with water.

$\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  and  $\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  were studied spectrophotometrically with the ethanol-chloroform mixture as the solvent, and the interferences from  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  were eliminated by adding 2 ml of  $\text{CH}_3\text{COOH}-\text{NH}_4\text{OH}$  buffer after Babko<sup>11</sup>, pH 5.5 (Fig. 1, spectra No 5—7); the buffer was added as the last component before diluting the mixture to volume. The samples of  $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$  were measured immediately after preparation,  $\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  and  $\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$  were allowed to stand for 10 minutes before measurement. The reference solutions were of the same composition, but did not contain the metal ion.

Coulometric titrations of  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  were accomplished with generated hypobromite. The system was constituted by a platinum generating electrode and an auxiliary carbon electrode, diameter 6 mm, submerged in the base electrolyte and separated from the analyzed solution by a frit. Amperostatic connection was used, the end point was indicated biamperometrically with a platinum bielectrode. The electric charge was measured on the integrating unit of the analyzer.

The  $\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$  stock solution for coulometric titrations was prepared by dissolving the appropriate amount of the chemical in the base electrolyte (12 g of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$  in 1000 ml of water). The hypobromite was generated by using electrolyte consisting of 12 g of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$  and 100 g of KBr in 1000 ml of water. The pH of the solution was adjusted to 8.6 with dilute HCl.

TABLE I  
Results of Elemental Analysis and Some Physicochemical Properties of the Dithiocarbamates

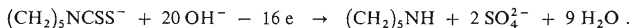
Compound (rel. molecular weight)	Crystal colour and shape	% Calculated (Found)						Solubility <sup>a</sup>
		M	C	H	N	S	O, Cl	
$\text{Na}_2\text{CN}(\text{CH}_2)_5 \cdot 2 \text{H}_2\text{O}$ (219.3)	white needles	10.48 (10.40)	32.86 (22.49)	6.43 (6.46)	6.38 (6.41)	29.24 (29.91)	14.61 (14.33)	WS, PS, WS, WS, WS
$\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$ (384.1)	brownblack	16.54 (16.45)	37.52 (37.54)	5.26 (5.31)	7.29 (7.19)	33.39 (33.58)	—	IS, S, PS WS, PS
$\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$ (379.2)	dark green	15.51 (15.78)	38.00 (38.36)	5.31 (5.55)	7.38 (7.14)	33.80 (33.17)	—	IS, S, PS,, S PS
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$ (536.6)	blackbrown	10.42 (10.85)	40.28 (39.86)	5.63 (5.61)	7.83 (7.69)	35.84 (35.09)	—	IS, WS, IS WS, S
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2 \text{Cl}^b$ (411.9)	black	13.55 (13.60)	34.98 (35.49)	4.89 (5.43)	6.79 (6.51)	31.13 (30.67)	8.60 (9.20)	IS, WS, PS, WS, S

<sup>a</sup> In water, chloroform, ethanol, 90% dimethylformamide, nad 80% acetic acid, respectively; WS well soluble, S soluble, PS partly soluble, IS insoluble; <sup>b</sup> prepared from  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ , recrystallized from chloroform.

## RESULTS AND DISCUSSION

*Coulometric Titrations of NaS<sub>2</sub>CN(CH<sub>2</sub>)<sub>5</sub>·2 H<sub>2</sub>O*

Total oxidation of dithiocarbamates brings about oxidation of sulfur as far as sulfates<sup>12</sup>. A convenient oxidant for NaS<sub>2</sub>CN(CH<sub>2</sub>)<sub>5</sub>·2 H<sub>2</sub>O is alkali hypobromite generated coulometrically from KBr on Pt electrode with constant current. The oxidation can be expressed as



The results of coulometric determination of NaS<sub>2</sub>CN(CH<sub>2</sub>)<sub>5</sub>·2 H<sub>2</sub>O are given in Table II; obviously, the method is suitable for the determination of small quantities of the substance, the error of determination does not exceed errors of routine coulometric determinations.

*Electronic Spectra*

Electronic spectra of NaS<sub>2</sub>CN(CH<sub>2</sub>)<sub>5</sub>·2 H<sub>2</sub>O in solutions exhibit a broad double band,  $\lambda_{\text{max}}$  approximately 262 and 280 nm. In addition, an absorption band can be observed in the spectra of more concentrated solutions ( $c > 3 \cdot 10^{-2} \text{ mol l}^{-1}$ ) at approximately 351 nm (Fig. 1, spectra No 8–10).

If the pH of the solutions is lowered below pH 6.5, the substance decomposes. A band is seen to appear and gradually grow at roughly 208 nm; it belongs to carbon disulfide<sup>13</sup>, which is formed on the decomposition of the dithiocarbamate. The bands at 262 and 280 nm decrease and vanish accordingly (Fig. 1, spectra No 5–7).

TABLE II

Results of Coulometric Titration of NaS<sub>2</sub>CN(CH<sub>2</sub>)<sub>5</sub>·2 H<sub>2</sub>O

Prepared μg	Found μg	n <sup>a</sup>	Confidence interval μg	Relative error %	Current intensity	
					gener. mA	ind. μA
30.80	31.90	8	±0.46	1.49	3.0	0.12
51.30	52.40	9	±0.63	1.22	3.5	0.12
102.50	104.20	9	±1.07	1.04	3.5	0.12
205.00	204.00	7	±1.89	0.92	3.5	0.12
512.40	503.70	5	±3.00	0.58	5.0	0.12

<sup>a</sup> Number of parallel measurements.

When organic solvents (dimethylformamide, acetonitrile, dimethyl sulfoxide, *etc.*) are used instead of water, the components of the doublet separate and, moreover, shift to longer wavelengths (Fig. 1, spectrum No 3). The bands are sensitive to the polarity of the solvent.

The band positions for the chelates studied are given and their interpretation is suggested in Table III. As is well known, the spectra of octahedral complexes of Fe(III), Mn(III), and Co(III) dithiocarbamates resemble each other closely. A higher number of absorption bands are found in the visible region, as can be seen from the data for  $\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$  given in Table III.

Very weak absorption bands due to the  $d-d$  transitions (crystal field bands), which could be expected for octahedral iron complexes at wavelengths above 660 nm, were actually observed only in acetic acid; in the other solvents they are overlapped by charge transfer bands. The low intensity and width of these bands points to forbidden spin transitions.

The absorption bands of the copper and nickel complexes at 620–640 nm (characteristic of  $d-d$  transitions) are accompanied by a band at 500–515 or 470–480 nm for the two complexes, respectively. These bands are associated with a crystal conversion of the Cu(II) or Ni(II) ion, and indicate planar geometry of the complexes.

### Infrared Spectra

The bands in the range of  $200-1600\text{ cm}^{-1}$  were recorded and partly characterized to elucidate the type of coordination and nature of the metal-ligand bond. From

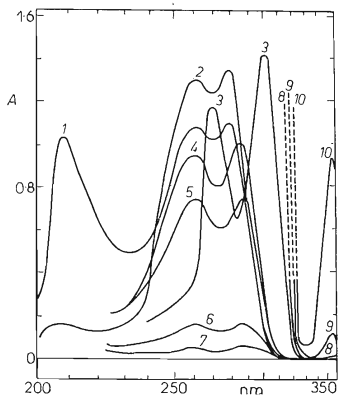


FIG. 1  
Absorption Spectra of  $\text{Na}_2\text{S}_2\text{CN}(\text{CH}_2)_5 \cdot 2\text{H}_2\text{O}$  in Various Solvents

1, 8, 9, 10 in water, 2 in 0.01M-NaOH, 3 in 90% dimethylformamide, 4–7 in ethanol-chloroform-water mixed solvent (6 : 1 : 3) 4 in the absence, 5–7 in the presence of buffer pH 5.5; 5 scanned immediately, 6 five minutes, 7 ten minutes after the addition of the buffer to the reaction system.

$c_{\text{Na}_2\text{S}_2\text{CN}(\text{CH}_2)_5 \cdot 2\text{H}_2\text{O}}$  ( $\text{mol l}^{-1}$ ): 1— $7.8 \cdot 10^{-5}$ , 8  $2 \cdot 10^{-2}$ , 9  $3 \cdot 10^{-2}$ , 10  $4 \cdot 10^{-2}$ .

TABLE III  
Electronic Spectra of the Dithiocarbamates in Various Solvents

Compound	Solvent	Intra-ligand transitions		Charge-transfer transitions				$d-d$ transitions		
		$M \rightarrow L$		$L \rightarrow M$		$\lambda_{\max}$ nm	$\log \epsilon$			
		$\lambda_{\max}$ nm	$\log \epsilon$	$\lambda_{\max}$ nm	$\log \epsilon$					
$\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$	$\text{CHCl}_3$	276	4.55	253	4.13	445	4.11	512	3.49	
		290	4.34						620	3.00
	M.S. <sup>a</sup>	273	4.51	246	4.07	438	4.09		504	3.60
		286	4.30						638	3.08
	DMFA <sup>b</sup>	274	4.60	—	—	—	440	4.18	507	3.56
		287	4.46						620	2.70
$\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$	$\text{CHCl}_3$	251	4.53	330	4.54	394	3.81	473	2.34	
						426	3.24	635	1.91	
	M.S. <sup>a</sup>	246	4.51	327	4.53	390	3.74	470	2.13	
						422	3.20	633	1.86	
	DMFA <sup>b</sup>	—	—	330	4.39	395	3.60	476	2.30	
						428	2.33	636	1.89	
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$	$\text{CHCl}_3$	269	4.59	315	4.09	513	3.40	—	—	
				351	4.04	592	3.21			
	$\text{CH}_3\text{COOH}^c$			388	3.93					
		263	4.60	307	4.31	452	3.94	712	3.30	
				356	3.92	498	3.80			
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2\text{Cl}$	$\text{CHCl}_3$	267	4.46	315	4.07	440	3.63	—	—	
				341	3.89	485	3.38			
				376	3.79	616	3.30			

<sup>a</sup> Mixed solvent ethanol-chloroform-water 6 : 1 : 3; <sup>b</sup> 90% dimethylformamide; <sup>c</sup> 80% acetic acid.

this point of view, three ranges of absorption bands are of interest. The first is the range of  $1450-1550\text{ cm}^{-1}$ , corresponding to the  $\text{C}\equiv\text{N}$  bond stretching vibrations. The position of the band at  $1500\text{ cm}^{-1}$  depends on the size of the substituents at the nitrogen atom, which indicates that this position is a function of both the degree of conjugation of the bonds within the molecule and of the structure of the entire molecule. The highest frequencies for the CN vibrations are generally found for dithiocarbamate complexes with central atoms of Ni(II) and Cu(II), and also Pt(II); this bears out the occurrence of a strong metal-sulfur chemical bond with planar structure of the coordination sphere, which has been also confirmed by X-ray structural analysis<sup>8,9</sup>.

TABLE IV  
Characteristic Absorption Bands in the Infrared Spectra of the Dithiocarbamates

Compound	Absorption band <sup>a</sup>			
	$\text{C}\equiv\text{N}$	$\text{N}-\text{C}\begin{matrix} \nearrow \text{S} \\ \searrow \text{S} \end{matrix}$	$\text{C}=\text{S}$	$\text{M}-\text{S}$
$\text{NaS}_2\text{CN}(\text{CH}_2)_5 \cdot 2\text{H}_2\text{O}$	1 460 s, br (1 420) w, sh	1 220 s 1 129 m 1 110 m	1 021 m, sh 1 003 m, sh 964 s 947 w, sh	379 w
$\text{Cu}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$	1 499 vs, br (1 438) s, sh	1 225 s 1 105 m	1 020 s, sh 992 m, sh 970 s 950 w, sh	352 s
$\text{Ni}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2$	1 506 vs, br (1 438) s, sh	1 235 s 1 113 m	1 022 s 998 s 975 m, sh 951 m, sh	388 s
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$	1 460 vs, br (1 439) w, sh	1 233 s 1 129 m	1 022 w, sh 1 000 s 979 m, sh 950 m, sh	361 s, br 347 s, sh
$\text{Fe}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2\text{Cl}$	1 440 vs, br	1 230 s 1 126 m	1 020 vw, sh 1 000 s 973 m, sh 949 m, sh	362 s, br 346 s, sh

<sup>a</sup> Position in  $\text{cm}^{-1}$ ; intensity: vs very strong, s strong, m medium, w weak, vw very weak; br broad, sh shoulder.

The second significant range,  $950-1050\text{ cm}^{-1}$ , is associated with  $\text{C}=\text{S}$  or  $\text{C}-\text{S}$  vibrations<sup>14</sup>. The presence of a single band in this range indicates according to the Ugo-Bonati criterion<sup>15</sup> totally symmetrical bond of the ligand to the metal, operating bidentately. The occurrence of two bands in this region is indicative of the presence of a complex-type ( $\text{C}=\text{S}$ ) and a noncomplex-type ( $\text{C}-\text{S}$ ) group, which implies that the ligand is bonded in the monodentate fashion. This Ugo-Bonati criterion is generally fairly reliable, since in this region a band splitting itself points to the presence of two non-equivalent CS bonds in a molecule<sup>14</sup>, but exceptions and some limitations exist<sup>14</sup>. As can be seen from Table IV, however, the complexes under study exhibit here not one or two bands, but as many as four, and moreover, additional characteristic bands at  $1060-1065$  and  $1260-1265\text{ cm}^{-1}$  are lacking, which indicates<sup>16,17</sup> that the presence of ligands bonded in the monodentate way is rather unlikely. Taking into account these findings we assume that the complexes involve non-equivalent ligands, whose effect manifests itself as vibrational coupling<sup>18</sup>. The position of these bands itself is to an extent dependent on the nature and oxidation degree of the central atom.

The absorption bands in the region of  $350-400\text{ cm}^{-1}$  correspond to the  $\nu(\text{M}-\text{S})$  vibrations of the chemical bonds<sup>14</sup>. The data on the infrared spectra of the complexes under study are given in Table IV.

#### *Stability Constants and Composition of the Complexes*

The solubility of the substances in question in various organic solvents or mixed solvents given in Tables I and V can be practically utilized for spectrophotometric determination of low quantities of  $\text{Cu(II)}$ ,  $\text{Ni(II)}$ , and  $\text{Fe(III)}$  as dithiocarbamate complexes. We considered it therefore theoretically as well as practically significant to examine the stability and composition of these complexes in the solvents of interest. The absorbances of the solutions of isomolar mixtures and the derived Job curves show that in the conditions applied (see Experimental and Table V),  $\text{Cu(II)}$  and  $\text{Ni(II)}$  react with the dithiocarbamate ligand in the molar ratio 1 : 2,  $\text{Fe(III)}$  in the molar ratio 1 : 3, a single complex species being formed. This was corroborated by the Vosburg-Cooper method<sup>19</sup> as well as by isolation and analysis of the crystalline preparations. The Job curves served for the calculation of the stability constants<sup>20</sup>, which are given in Table V along with the molar absorptivities  $\epsilon$  obtained as averages from thirty absorbance values measured by the differential method.

#### *Analytical Use of the Dithiocarbamate Complexes*

The dependence of absorbance on the concentration was measured using 1 cm cells in order to test the validity of the Lambert-Beer law. In a concentration region the calibration curve is linear and passes through the origin, hence no additional absorbing substances occur in the solution. A 5-10% excess of the ligand over the



TABLE V  
Stability Constants of the Complexes and Some Data for Spectrophotometric Determination of Cu(II), Ni(II), and Fe(III)

Complex	Solvent	$\lambda_{\text{max}}$ nm	$\log \epsilon$ $\text{l mol}^{-1} \text{cm}^{-1}$	$\log \beta_2$ ( $\log \beta_3$ )	Limit of determination $\text{g ml}^{-1}$	Upper limit of validity of the Lambert-Beer law $\text{g ml}^{-1}$
Cu[S <sub>2</sub> CN(CH <sub>2</sub> ) <sub>5</sub> ] <sub>2</sub>	M.S. <sup>a</sup>	273	4.51	13.20	$8.2 \cdot 10^{-8}$	$2.5 \cdot 10^{-6}$
	DMFA <sup>b</sup>	438	4.09	12.65	$2.1 \cdot 10^{-7}$	$2.5 \cdot 10^{-6}$
		440	4.18		$3.2 \cdot 10^{-8}$	$2.5 \cdot 10^{-6}$
Ni[S <sub>2</sub> CN(CH <sub>2</sub> ) <sub>5</sub> ] <sub>2</sub>	M.S. <sup>a</sup>	246	4.51	12.39 12.25 <sup>c</sup>	$7.5 \cdot 10^{-8}$	$2.3 \cdot 10^{-6}$
	DMFA <sup>b</sup>	327	4.53		$7.0 \cdot 10^{-8}$	$2.3 \cdot 10^{-6}$
		395	3.60		$3.0 \cdot 10^{-7}$	$2.3 \cdot 10^{-6}$
Fe[S <sub>2</sub> CN(CH <sub>2</sub> ) <sub>5</sub> ] <sub>3</sub>	CH <sub>3</sub> COOH <sup>d</sup>	452	3.94	(14.85)	$5.5 \cdot 10^{-7}$	$5.5 \cdot 10^{-6}$

<sup>a</sup> Mixed solvent ethanol-chloroform-water 6 : 1 : 3; buffer, pH/ 5.5, was added (2 ml in 25 volumetric flask) to eliminate interference from Na<sub>2</sub>CN(CH<sub>2</sub>)<sub>5</sub>·2 H<sub>2</sub>O; <sup>b</sup> 90% dimethylformamide; <sup>c</sup> 12.60 according to ref. <sup>6</sup>; <sup>d</sup> 80% acetic acid.

metal is tolerable; solutions with higher excess of the ligand are turbid, which makes the measurement difficult. The measurements were performed using reference solutions containing the same components as the sample but without the metal ion.

The limit of determination was obtained by applying the calibration curve method<sup>21</sup> for 99% probability from twenty absorbance values of the blank. The upper limits of validity of the Lambert-Beer law, limits of determination of Cu(II), Ni(II), and Fe(III), as well as the measurement conditions are given in Table V.

The reproducibility of the method was tested with a higher number of model samples. The results showed that under the conditions applied the method can be used for trace analysis. The errors of the individual determinations did not exceed the limit of error commonly resulting during spectrophotometric determination of small quantities of substances.

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