

**SPECTROPHOTOMETRIC CHARACTERISTICS OF THALLIUM(III) COMPLEXES WITH IODOACETIC ACID AND TERTIARY AMINES****Dragan S. Mihajlović<sup>1</sup> and Trajče Stafilov<sup>2</sup>**<sup>1</sup>*A.D. Tehnička kontrola, 91000 Skopje, Republic of Macedonia*<sup>2</sup>*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, The “Sv. Kiril & Metodij” University, P.O. Box 162, 91001 Skopje, Republic of Macedonia*

New method for spectrophotometric determination of thallium in the presence of large amount of cadmium is described. This method is developed on the basis of the investigation of thallium(III) complexes with iodoacetic acid and ternary amines. The complexes are soluble in water and/or in organic solvents and show an absorption peak at 365–405 nm, depending upon the amine and solvent used. For a practical application, hexamethylenetetramine and pyridine was used as an organic base. The spectra of the solutions of In(III), Ga(III), Cd(II) and Zn(II) in the presence of CH<sub>2</sub>ICOOH and tertiary amines do not have an absorption band in the spectral region above 320 nm. It may be utilized for spectrophotometric determination of thallium in presence of large amount of these elements. The molar absorption coefficient of the complex of thallium with iodoacetic acid and hexamethylenetetramine is about 4500 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup> in isobutylmethyl ketone and isoamylacetate and 6000 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup> in propanol-water mixture (1+2), while the complex with pyridine has a molar absorption coefficient 5800 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>. Spectrophotometric method for determination of thallium in cadmium metal by iodoacetic acid and pyridine was developed. For content of thallium between 0.05 and 0.15 %, average standard deviation was 0.0016 % Tl, while between 0.15 and 0.40 % Tl standard deviation was 0.0022 %.

**Keywords:** thallium; determination in cadmium; spectrophotometry; ternary complexes; iodoacetic acid; hexamethylenetetramine; pyridine

**INTRODUCTION**

A literature search on the spectrophotometric determination of thallium showed that, in the past decade, very few methods have been published. Usually, ternary complexes are used, in which Tl<sup>3+</sup> enters as a halogenothallate, mostly [TlCl<sub>4</sub>]<sup>-</sup>, while the second ligand is one of the known spectrophotometric reagents: crystal violet [1], cresyl violet [2], pyronine G [3], rhodamine B [4], safranin T [5] etc. If new sensitive reagents are involved, they are usually commercially unattainable, as 2,6-dibromo-4-sulfamoylphenylazo-aminoazobenzene [6], 2-[1-(5-dimethylaminothienyl-2)-vinyl-2]-1,3,3-trimethyl-3N-indolium [7] etc.

Ternary complexes of thallium, in which as a second ligand an organic base participates, has been known for a long time. The most often used is triisooctylamine [8] or tri-n-octylamine [9].

It is well known that thallium forms stable carboxylates [10]. The thallium acetates are much stronger electrophiles than the halides, and take a part in many organic reactions [11]. However, acetic acid and its halogen derivatives are not used as complexing reagents for spectrophotometric determination of thallium, although chloro derivatives of acetic acid have been examined as complexing ligand for other elements.

In our previous article [12] we introduced iodoacetic acid and hexamethylenetetramine as complexing reagents for determination of thallium in zinc metal. This paper is concerned with a study of some spectrophotometric characteristics of complexes of thallium(III) with CH<sub>2</sub>ICOOH and some tertiary amines, and with a develop of a spectrophotometric method for determination of thallium in cadmium metal, also.

## EXPERIMENTAL

*Instrumentation*

UV/VIS spectra were recorded on HP 8452 Diode Array spectrophotometer. For determination of thallium in samples of cadmium metal, used for a checking the accuracy of the proposed spectrophotometric method, Varian SpectrAA 640Z atomic absorption spectrometer (AAS), ARL 3460 optical emission spectrometer (OES) and ARL 8480 X-ray fluorescent spectrometer (XRF) were used.

*Reagents and samples*

All inorganic reagents were p.a. grade. The solution of iodoacetic acid was preliminary treated by n-heptane or other suitable solvent for extraction of free iodine, usually present in commercial products.

The organic solvents were p.a. grade, while some amines were *for synthesis* grade. For determination of thallium in cadmium, spectrophotometric grade pyridine was used.

Standard solution of thallium was prepared by dilution of commercial solution of  $Tl(NO_3)_3$ . The solution was freshly oxidized by  $Br_2$ , and the excess of bromine was expelled by evaporation.

For simulation of cadmium matrix, a spectrographically pure cadmium metal (JMC 170, John-

son Matthey Chemicals, London), prepared in form of sponges, was used.

*Procedure for a spectrophotometric determination of thallium in cadmium metal*

Decompose 0.2000 g of sample with 15 ml of diluted (1+3) nitric acid in 150 ml beaker. Heat the beaker to assist the decomposition. After dissolution, add 2–3 drops bromine, or 5 ml saturated bromine water and boil the solution to oxidize thallium to  $Tl^{3+}$ . Boil gently until wet salts appear. Add 5 ml water and repeat heating. Cool and dissolve the salts into 5 ml water. Transfer the solution into 25 ml volumetric flask, wash the beaker with 5 ml 0.1 mol/l solution of iodoacetic acid and with 8–9 ml water, transfer into the flask and add 5 ml pyridine. Allow to stand 10 min, and make up the volume to 25 ml with water. Measure the absorbance at 400 nm against a blank solution of iodoacetic acid (0.02 mol/l).

*Preparation of calibration curve.* Transfer 7 weights of 0.2 g pure cadmium metal into 150 ml beakers. Take suitable aliquots of standard solution of thallium to cover the range from 100 to 700  $\mu g$  Tl, and transfer into the beakers. Add 15 ml nitric acid and continue as it is described above.

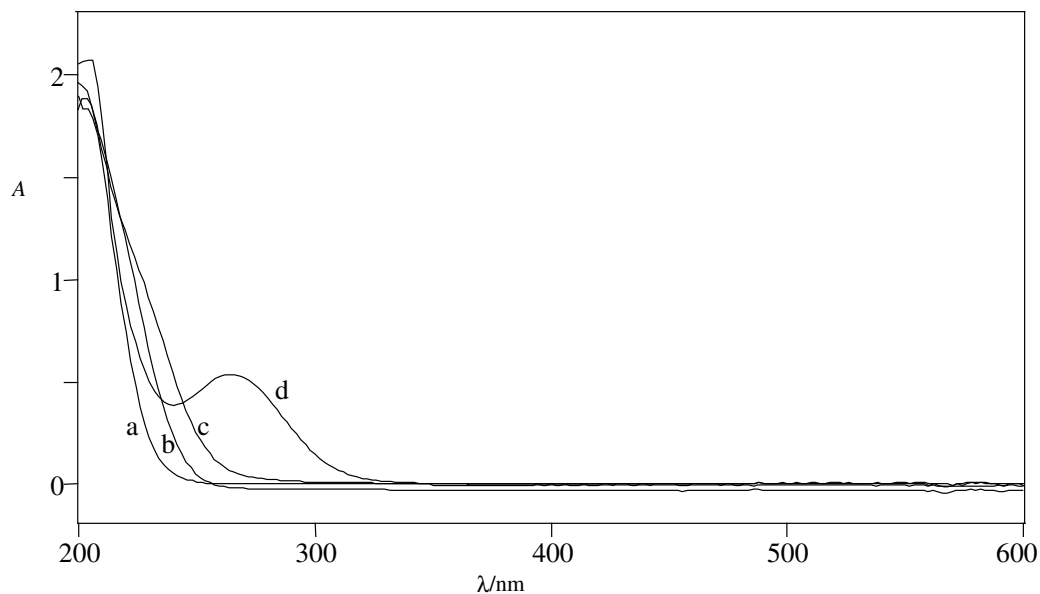
## RESULTS AND DISCUSSION

*1. UV/VIS spectra of halogen derivatives of acetic acid*

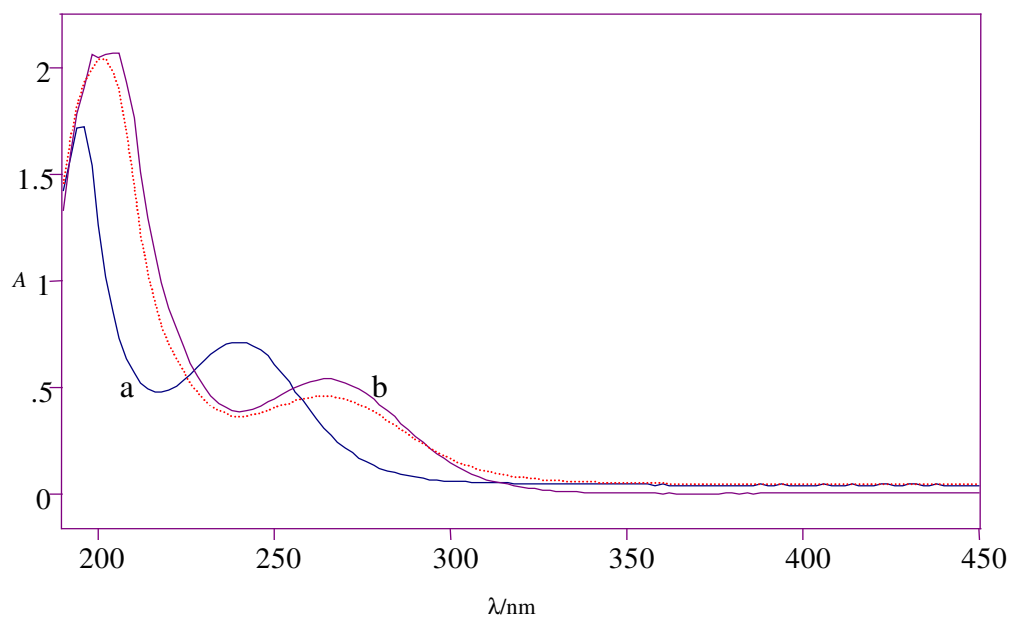
UV/VIS spectra of aqueous solutions of  $CH_2ClCOOH$ ,  $CCl_3COOH$ ,  $CH_2BrCOOH$  and  $CH_2ICOOH$  are shown in Fig. 1. The spectrum of  $CH_2ICOOH$  differs from the spectra of the chloro and the bromo analogues: in the spectrum of iodoacetic acid a band with a peak at 264 nm occurs. This band is a result of  $n \rightarrow \sigma^*$  transition of lone pairs electrons on iodine atom [13]. The position of this peak depends, in some measure, upon the polarity of the solvent:  $\lambda_{max} = 276$  nm in acetonitrile, 264 nm in cyclohexanol, 269 nm in ethanol and 264 nm in water.

*2. Reaction of iodoacetic acid with cations*

The characteristics of the complexes of some metals with haloacetic acids are published in literature. Complexes of Cu [14], Fe [15], Y, La, Ce [16], Co [17], and other metals with iodoacetic acid are known for a long time. Our investigation showed that Tl(III) forms acido complex with iodoacetic acid, also. This can be seen from the changes in the spectra of the solutions of its salts. Thus, in the spectrum of the solution of  $TlCl_3$ , band with peak at 240 nm occurs. But, if a solution of iodoacetic acid is added to the neutral solution of  $TlCl_3$ , the mentioned band disappears, which means that  $Cl^-$  anions from the ligand sphere of the halocomplex of Tl are substituted by  $CH_2ICOO^-$ . In Fig. 2, the spectra of the solutions of  $TlCl_3$  (spectrum a) and  $TlCl_3 + CH_2ICOOH$  (spectrum b) are given.



**Fig. 1.** UV/VIS spectra of halogen derivatives of acetic acid: chloroacetic acid (a), trichloroacetic acid (b), bromoacetic acid (c) and iodoacetic acid (d)



**Fig. 2.** UV/VIS spectra of solutions of  $TlCl_3$  (a) and solutions of  $TlCl_3$  plus iodoacetic acid (b). UV/VIS spectrum of iodoacetic acid (dotted line)

The solution of iodoacetic acid remains colorless in a presence of  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $In^{3+}$ ,  $Ga^{3+}$ ,  $Al^{3+}$  and  $Tl^{3+}$ .  $Fe^{3+}$  forms an acido complex with faint yellow color, but after addition of organic base, a brown colloidal precipitate is formed.  $Cu^{2+}$

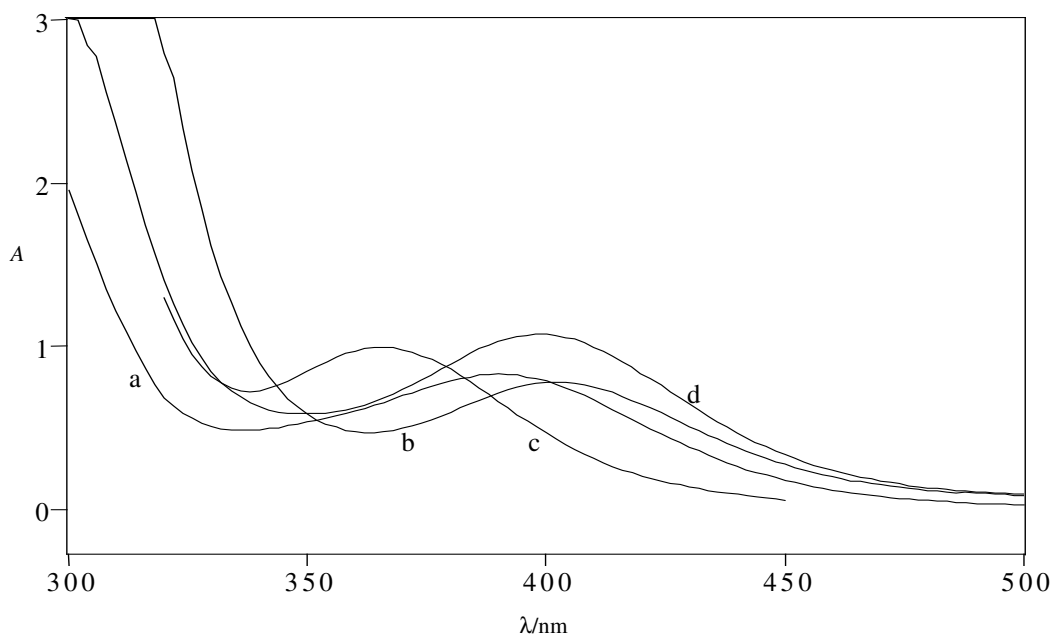
also gives a dark precipitate after addition of amine.  $Pb^{2+}$  in high concentration ( $1 \text{ mg/cm}^3$ ) gives heavy yellow precipitate after addition of HMTA. Though these precipitates are not extractable in organic solvents, it is desirable that the total con-

tent of Fe, Cu and Pb do not extend  $1 \text{ mg/cm}^3$ . For a higher content of these elements, prior separation is necessary.

### 3. Formation of ternary complexes of $\text{Tl}^{3+}$ with iodoacetic acid and tertiary amines

Based on the presumption of the formation of an acido complex of thallium with iodoacetic acid, it can be expected that the absorption band at 265 nm in the spectrum of this complex (in aqueous solution), as the only band in the spectrum above 250 nm, may serve for spectrophotometric purposes if an organic base is introduced as a second, bathochrome ligand. Primary and secondary amines can not serve for this purpose, due to the reaction of

neutralization with  $\text{CH}_2\text{ICOO}^-$  anions. But, tertiary amines show an influence on this band, forming ternary complexes. So, pyridine, quinoline, pyrimidine and pyrrole give yellow ternary complex. However, in the presence of piperidine, aminopyridine, aminoquinoline, pyrrolidine, dimethylamine and other primary and secondary aliphatic and aromatic amines, the solution of the acido complex of thallium with iodoacetic acid remains colorless. The effects of addition of tertiary amines are manifested on the shift of the mentioned band in the spectrum of iodoacetic acid at 264 nm for 100–140 nm. The spectra of the complexes of thallium(III) with iodoacetic acid and some amines are shown in Fig. 3.



**Fig. 3.** UV/VIS spectra of ternary complexes of thallium with iodoacetic acid and tertiary amines: hexamethylenetetramine (a), pyridine (b), quinoline (c) and tri-n-octylamine (d).

For practical application, hexamethylenetetramine (HMTA) was chosen for further investigation. HMTA is a stable substance, soluble in water. Solution of HMTA is transparent for light above 200 nm. The spectrum of the complex of Tl with iodoacetic acid and HMTA recorded in chloroform and carbon tetrachloride has  $\lambda_{\text{max}}$  at 370 nm, in isoamyl acetate, isobutyl alcohol, amyl alcohol and isobutylmethyl ketone at 400–405 nm.

### 4. Determination of the composition of the acido complex of thallium with iodoacetic acid

The ratio of thallium to iodoacetic acid in the acido complex was determined by mole ratio method [18]. The results show that a complex with ratio of Tl to iodoacetic acid 1:4 is formed ( $[\text{Tl}(\text{CH}_2\text{ICOO})_4]^-$ ). The number of HMTA molecules that participate in the tertiary complex was not done by this method with enough certainty.

Pyridine as a ligand participate with 4 molecules in the complex.

### 5. Molar absorption coefficient ( $\epsilon$ ) of the complex of Tl with iodoacetic acid and HMTA

The complex of thallium(III) with iodoacetic acid and HMTA in aqueous solution has a molar absorption coefficient  $4500 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ . If the formation of the complex is done in an aqueous-organic media, an increase or decrease of absorbance of the complex can occur. The molar absorption coefficients of the complex, formed in different aqueous : organic mixtures are shown in Table I.

Table I

*Molar absorption coefficients of the complex of  $\text{Tl}^{3+}$  with iodoacetic acid and HMTA, formed in different organic : water media*

Organic component	Optimal volume ratio organic component : water	Molar absorption coefficient
Acetone	1 : 4	4100
1,2-propandiol	1 : 4	4600
1,2-butandiol	1 : 4	4600
Glycol	1 : 2	4850
Ethanol	1 : 2	4700
Isopropanol	1 : 2	6000

Dioxane, added to the solution of  $\text{Tl}^{3+}$ , has a negative influence on the complex formation. 1,2-propandiol and 1,2-butandiol insignificantly increase the absorbance, while triethanolamine totally prevents the formation of the complex. Maximal positive effect shows isopropanol. In isopropanol-water mixture (1+2), the highest molar absorption coefficient of the complex is achieved, higher than in organic extracts.

Significantly lower values of molar absorption coefficient of the complex extracted in chloroform and carbon tetrachloride suggests that in these solvents concurrent reactions between HMTA and chlorine atom from the solvent occur. After ten minutes the yellow color of the complex in these solvents disappears. The complex couldn't be extracted with cyclohexane. In nonpolar solvents, as

benzene, toluene etc.,  $\epsilon$  has low values, also. The molar absorption coefficients of the complex, extracted in different solvents, are shown in Table II.

Table II

*Molar absorption coefficients of the complex of  $\text{Tl}^{3+}$  with iodoacetic acid and HMTA, extracted into different organic solvents*

Solvent	$\epsilon / \text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$
Isoamylacetate, isopropylacetate	4300
Benzene, xylene	1800
Methyl isobutil ketone	4400
Diisopropyl ether	4300
Cyclohexane	0
Carbon tetrachloride, chloroform	2000
Isoamyl alcohol, isobutil alcohol	2500

### 6. Rate of the formation of ternary complex of $[\text{Tl}(\text{CH}_2\text{ICOO})_4]^-$ and tertiary amines

The reaction of formation of the ternary complex of thallium with iodoacetic acid and HMTA is relatively slow and, depending on the concentration of the reagents, is practically finished in 20 minutes. After this period, the absorbance of the complex remains constant.

However, the reaction of  $[\text{Tl}(\text{CH}_2\text{ICOO})_4]^-$  with pyridine is practically instantaneous.

### 7. Application

The fact that Zn doesn't forms ternary complex with iodoacetic acid and HMTA was utilized for the determination of thallium content in zinc metal [12]. A similar procedure, using pyridine instead HMTA, is applied for determination of thallium in cadmium metal.

As it was mentioned, cadmium doesn't form complexes with iodoacetic acid and pyridine. On Fig. 4, UV/VIS spectra of solution of  $\text{CdSO}_4$ ,  $\text{CdSO}_4$  + iodoacetic acid and  $\text{CdSO}_4$  + iodoacetic acid + pyridine are shown. A broad and intensive band, which is result of the pyridine absorption, stretches up to 350 nm and doesn't influence on the thallium complex absorption at 400 nm. It was utilized for spectrophotometric determination of thallium in technical cadmium.

Data, obtained for the construction of calibration curve (described in the Experimental section),

are shown in Table III.

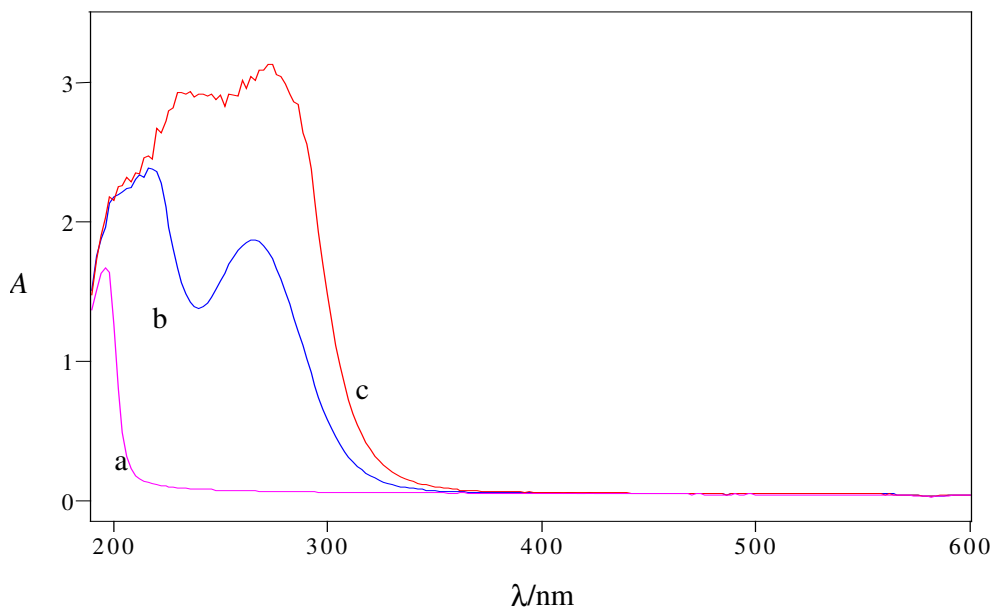


Fig 4. UV/VIS spectra of solution of CdSO<sub>4</sub> (a), CdSO<sub>4</sub> + iodoacetic acid (b) and CdSO<sub>4</sub> + iodoacetic acid + pyridine (c)

Table III

*Experimental data used for construction of calibration curve for spectrophotometric determination of thallium in cadmium by iodoacetic acid and pyridine*

μg Tl, added to 200 mg Cd	0	100	200	300	400	500	600	700
$w_{\text{Tl}}(\% \text{ m/m})$	0	0.05	0.100	0.150	0.200	0.250	0.300	0.350
Absorbance	0.032	0.134	0.251	0.377	0.448	0.582	0.663	0.754

From this data, the next equation of the calibration curve was obtained:

$$w_{(\text{Tl})}(\%, \text{ m/m}) = 0.0949A^2 + 0.3645A - 0.0002 \quad (1)$$

where  $A$  denotes absorbance.

Due to the lack of certified reference samples, the proposed method was checked by analysis of selected cadmium samples, in which the thallium content was determined by flame AAS. The same samples were also analyzed by OES and XRF spectrometry, but due to the mentioned lack of standards for calibration of these instruments, the results of analyses haven't been taken into a consideration. Only intensities of the analytical signals for

thallium were utilized from these methods. The results are shown in Table IV.

Table IV

*Intensities of analytical signals of thallium from selected cadmium samples, obtained by OES (col. 2), XRF (col. 3) and proposed spectrophotometric method (col. 4). Results of the analysis of the same samples by AAS (col. 5) and UV/VIS (col. 6)*

Sample No.	$I_{\text{OES}}$ (mV)	$I_{\text{XRF}}$ (counts/s)	$w_{\text{Tl}}$ (% m/m) AAS	$cw_{\text{Tl}}$ (% m/m), by proposed method	$A_{(\text{UV/VIS})}$
Cd-1	26	138	0.021	0.014	0.056
Cd-2	173	271	0.105	0.113	0.286

Cd-3	282	353	0.168	0.165	0.389
Cd-4	449	484	0.261	0.271	0.623
Cd-5	655	725	0.376	0.383	0.845

The correlation coefficients between the corresponding intensities of the analytical signals for samples Cd-1 to Cd-5, obtained by OES (mV) and XRF (counts/s) and absorbances, obtained by proposed spectrophotometric method were  $r_{(\text{OES-UV/VIS})} = 0.9975$  and  $r_{(\text{XRF-UV/VIS})} = 0.9900$ . The correlation coefficients between OES and XRF intensities and

the content of thallium, determined by AAS were  $r_{(\text{OES-AAS})} = 0.9995$  and  $r_{(\text{XRF-AAS})} = 0.9953$ .

The average of the absorbance of the blank sample (solution of cadmium chloride, iodoacetic acid and pyridine) was 0.029 with a corresponding standard deviation  $\text{SD}_{\text{blank}} = 0.0012$ .

The standard deviations, obtained by 11 analysis of samples Cd-2 and Cd-5, were 0.0016 and 0.0022.

The detection limit, calculated using  $A_{\text{blank}} + 3 \text{SD}_{\text{blank}}$ , was found to be 0.011 % Tl or 0.8  $\mu\text{g}$  Tl/ml.

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#### Резиме

### СПЕКТРОФОТОМЕТРИСКИ КАРАКТЕРИСТИКИ НА ТАЛИУМ(III) КОМПЛЕКСИ СО ЈОДОЦЕТНА КИСЕЛИНА И ТЕРЦИЕРНИ АМИНИ

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**Клучни зборови:** талиум; определување во кадмиум; спектрофотометрија; тернерни комплекси; јодоцетна киселина; хексаметиленететрамин; пиридин

Талиум(III) формира ацидокомплекси со јодоцетната киселина, кои даваат жолти тернерни комплекси со терциерни амини. Комплексите се растворливи во вода и/или во органски растворувачи и даваат лента со максимум на 365–405 nm, зависно од употре-

бениот амин. За практична примена се користени хексаметиленететрамин и пиридин како органски бази. Спектрите на растворите на In(III), Ga(III), Cd(II) и Zn(II) во присуство на CH<sub>2</sub>ICOOH и терциерни амини немаат апсорпциона лента во областа над 320 nm. Ова

може да се искористи за спектрофотометриско определување на талиум во присуство на големи количества од овие елементи. Моларниот апсорпционен коефициент на талиумот со јодооцетната киселина и хексаметилентетрамин е околу  $4500 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$  во изобутил кетон и изоамил ацетат и  $6000 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$  во присуство на смеса од пропанол-вода (1+2), додека комплексот со пиридинот има моларен апсорпционен

коефициент од  $5800 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ . Со примена на овие испитувања развиен е спектрофотометриски метод за определување на талиум во кадмиум со примена на јодооцетна киселина и пиридин. За содржина на талиум од 0,05 до 0,15 % е добиена стандардна девијација од 0,0016 %, додека за содржина на талиум од 0,15 до 0,40 % стандардната девијација изнесува 0,0022 %.