

## ORIGINAL PAPER

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**Spectrophotometric determination of thallium in zinc and zinc-base alloys with iodoacetic acid and hexamethylenetetramine**

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**Abstract.** Thallium(III) forms a ternary complex of yellow colour with iodoacetic acid and organic bases, especially hexamethylenetetramine. The complex is soluble in water and various organic solvents. Zinc, copper, cadmium and iron do not form complexes with these reagents, so that a spectrophotometric determination of thallium in zinc and its alloys is possible. The limit of detection is  $15 \mu\text{g g}^{-1}$ , the molar absorption coefficient about  $2000 \text{ mol}^{-1} \text{ l}^{-1} \text{ cm}^{-1}$ .

**Introduction**

Ternary complexes of metal cations with acido ligands and organic bases are well known [1, 2]. Also, the halogen derivatives of acetic acid as acido complexing agents were investigated by several authors [3, 4]. During our examination of the characteristics of the acido complexes of thallium with halogen derivatives of acetic acid, it was found that Tl(III) forms a ternary complex with iodoacetic acid as an acido ligand and organic bases, such as pyridine, hexamethylenetetramine (HMTA), etc. The complex has an intensive yellow colour, is soluble in water and can be easily extracted by different organic solvents. It was found that chloro and bromo derivatives of acetic acid do not form coloured ternary complex with Tl(III) and HMTA, and Tl(I) generally does not form any coloured complexes with halogen derivatives of acetic acid and HMTA.

Thallium is usually present in technical zinc and zinc alloys, due to its occurrence in sulfide zinc ores. In zinc base alloys, thallium was determined spectrophotometri-

cally by several authors [5, 6]. We found that zinc, as a matrix element, and also elements usually present in commercial zinc alloys, do not form coloured complexes (or do not form complexes at all) with iodoacetic acid. This fact has been utilized to work out a new spectrophotometric method for the determination of thallium in zinc and zinc alloys.

**Experimental**

**Instrumentation.** The absorption spectra were recorded on a Hewlett Packard 8452 Diode Array spectrometer, while the absorbance measurements were carried out on a Pye Unicam SP 6-500 spectrophotometer.

**Stock solution of thallium.** A commercial standard solution of thallium, containing 1 g of Tl in form of  $\text{TlNO}_3$ , was oxidized with several drops of bromine. The solution was evaporated nearly to dryness (to expel the excess bromine) and the residue was diluted to 1000 ml with distilled water. Working solutions of Tl(III) were prepared by suitable dilutions.

**Zinc base samples.** For simulation of a zinc alloy matrix, spectrographically pure zinc rod (Matthey Standard JM 150, London) was prepared in form of sponges. Because of lack of reliable reference materials of zinc with certified values of thallium content, several samples of zinc from different manufacturers were analyzed by atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) spectrometry [7]. From these samples, sponges for checking the validity of the calibration curve were prepared.

**Preparation of the complex for preliminary investigations.** For preliminary investigations of the spectrophotometric characteristics, the ternary complex of thallium(III) was prepared as follows: Into a separatory funnel 5 ml of thallium solution were added containing  $100 \mu\text{g}$  of Tl(III). Then 5 ml of 0.1 mol/l iodoacetic acid solution and 5 ml of 0.1 mol/l HMTA solution were added. After 30 min, the complex was extracted with 10 ml of isoamyl acetate.

**Recommended analytical procedure.** Weigh 1.000 g of zinc sample and transfer into a 150 ml beaker. Add 25 ml of diluted hydrochloric acid (6 mol/l) and cover the beaker immediately with a watch glass. Heat on a hot plate to a complete dissolution of the sample. Add 5 ml of 0.5 mol/l ammonium persulphate solution, heat to boiling

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and keep at this temperature for 4–5 min for decomposition of the excess of oxidizing agent. Then carefully heat the solution until wet salts appear, add 5 ml of water and evaporate again to wet salts.

Dissolve the residue in 10 ml of water and transfer into a separatory funnel. Wash the beaker with 5 ml of water and transfer into the funnel. Then wash with 5 ml of 0.1 mol/l iodoacetic acid solution and repeat the washing with 5 ml of 0.1 mol/l HMTA solution. Mix the contents of the funnel and allow to stand for 30 min. Add exactly 10 ml of isoamylacetate and shake vigorously for 30 s.

Transfer a part of the extract carefully (best through a filter paper, previously wetted by isoamyl acetate) into a 1 cm glass cell and cover it. Measure the absorbance at 396 nm.

## Results and discussion

### Absorption spectrum of the complex

The absorption spectrum of the ternary complex of Tl(III) with iodoacetic acid and HMTA in aqueous solution was recorded from 240 to 520 nm. It has a maximum absorbance at 390 nm (Fig. 1a), while the spectrum of free iodoacetic acid shows a strong band below 300 nm (Fig. 1b). This is also present in the spectrum of the complex, due to an excess of iodoacetic acid used for its formation.

The absorption maximum of the ternary complex is slightly shifted when recorded in an organic solvent: to 396 nm in isoamyl acetate (Fig. 2a) and to 372 nm in chloroform (Fig. 2b). The strong band below 300 nm in both spectra originates from the absorption of a  $\sigma$  I-C bond in iodoacetic acid (both free acid, extracted from excess of reagents, and in the complex).

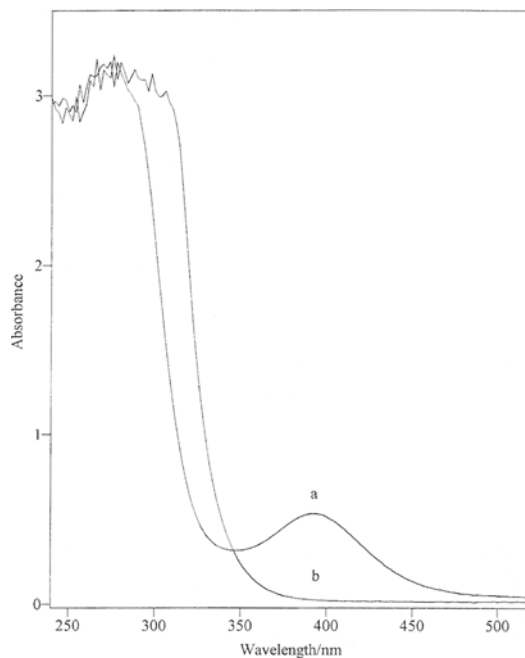
### Kinetics of the complex formation and its stability

The required time for formation of the complex was examined by measuring the absorbance of extracts of the complex, taken at different time intervals after addition of the complexing agents. The results showed that the rate of the ternary complex formation depends on the rate of the reaction between Tl(III) and iodoacetic acid. It was concluded that the extraction must be performed at least 30 min after addition of all reagents.

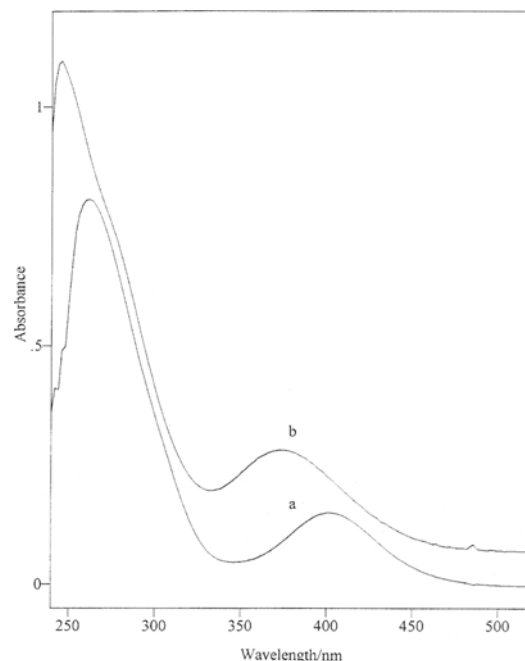
The absorbance of the complex remained constant for at least 24 h.

### Effect of hydrochloric acid

The influence of hydrochloric acid, which remains after dissolution of the sample, was examined by addition of this acid to the solution, containing 100  $\mu$ g of Tl( $m_{\text{Tl}}$ (added) in Table 1), before addition of the complexing agents. The absorbance of the complex, extracted in isoamyl acetate, was measured at 396 nm in a 1 cm glass cell. The mass of thallium, extracted as a complex, was calculated from the calibration curve (Eq. 1). The results are shown in Table 1.



**Fig. 1** Absorption spectrum of the ternary complex of thallium(III) with iodoacetic acid and HMTA (a) and spectrum of iodoacetic acid (b) recorded in aqueous solution



**Fig. 2** Absorption spectra of the ternary complex of Tl(III)-iodoacetic acid-HMTA recorded in isoamylacetate (a) and chloroform (b)

It is evident that hydrochloric acid must be expelled after the dissolution of the zinc sample. Evaporation to wet salts is enough to reduce the concentration of HCl to less than 0.1 mol/l in the final volume

(about 20 ml), in which the formation of the complex is performed.

#### Effect of diverse cations

The influence of different cations, which may be present in the solution after dissolution of zinc samples (especially samples of zinc alloys), was examined by addition of the cations (as suitable salts) to a solution containing 1 g of Zn and 500  $\mu\text{g}$  of Tl(III), before addition of the complexing agents. The quantities of diverse cations, which did not cause any change of the ratio  $m_{\text{Tl}}(\text{found})/m_{\text{Tl}}(\text{added})$  of more than 2%, are given in Table 2.

#### Calibration graph

For constructing the calibration graph 50, 100, 200, 300, 400, 500 resp. 600  $\mu\text{g}$  Tl were added to solutions

**Table 1** Effect of free hydrochloric acid on the complex formation

Final concentration of HCl (mol/l)	$m_{\text{Tl}}(\text{found})/m_{\text{Tl}}(\text{added})$
0.05	1.00
0.10	1.00
0.20	0.98
0.30	0.96
0.50	0.90
1.00	0.72

**Table 2** Tolerance limits for diverse cations

Cation	Allowed quantity of cation, mg
Mn <sup>2+</sup>	10
Cu <sup>2+</sup>	50
Fe <sup>2+</sup>	50
Ni <sup>2+</sup>	70
Pb <sup>2+</sup>	100
In <sup>3+</sup>	200
Cd <sup>2+</sup>	1000
Al <sup>3+</sup>	1000

**Table 3** Data obtained by the proposed method and by AAS and ICP

Sample No	Content of Tl (%) determined by ICP	Content of Tl (%) determined by AAS	Content of Tl (%) determined by the proposed method <sup>a</sup>
1	0.005	0.005	0.004
2	0.007	0.008	0.008
3	0.015	0.017	0.018
4	0.029	0.028	0.026
5	0.057	0.054	0.055
6	0.081	0.082	0.085

<sup>a</sup> Each value is the average of three parallel results

prepared by dissolution of samples of 1 g of spectrographically pure zinc. The solutions were evaporated twice to wet salts and the procedure was continued as described above.

Linear regression analysis gives the following equation for the calibration curve:

$$m_{\text{Tl}} = 1014.6 A + 4.92 \quad (1)$$

where  $m_{\text{Tl}}$  denotes the mass of thallium in  $\mu\text{g}$ , A the absorbance.

#### Checking the method

The method was checked by analyzing samples of zinc by means of AAS and ICP spectrometry [7]. Results are given in Table 3.

As can be seen, the contents of thallium obtained by the proposed method are very similar to those obtained by AAS and ICP.

Samples No. 1 and 5 were analyzed eleven times to calculate the standard deviation. For sample No. 1 the absolute standard deviation was  $s = 0.0010\%$ , for sample No. 5,  $s = 0.0022\%$ .

Eleven samples of 1.000 g of spectrographically pure zinc with the addition of 100 mg of  $\text{Cu}^{2+}$  and 100 mg of  $\text{Fe}^{2+}$ , but without addition of thallium, were analyzed for the calculation of the standard deviation of the blank sample. The average value of  $A_{\text{blank}}$  was 0.0046 with the corresponding value of the standard deviation of the absorbance of the blank sample  $S_{\text{blank}} = 0.0019$ .

The value of absorbance, which is for three  $S_{\text{blank}}$  greater than  $A_{\text{blank}}$ , is  $A_{\text{min}} = 0.010$ . The detection limit (LD) was calculated from  $A_{\text{min}}$  using the calibration Eq. (1):

$$\text{LD}_{\text{Tl}} = 1014.6 A_{\text{min}} + 4.92 = 15 \mu\text{g}$$

#### Conclusion

The results confirm that thallium(III) forms a ternary complex with iodoacetic acid and hexamethylenetetramine, yielding a yellow colour. The complex is soluble in water and many organic solvents. Zinc, copper,

cadmium and iron do not interfere, so that it can be utilized for the spectrophotometric determination of thallium in zinc and its alloys.

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