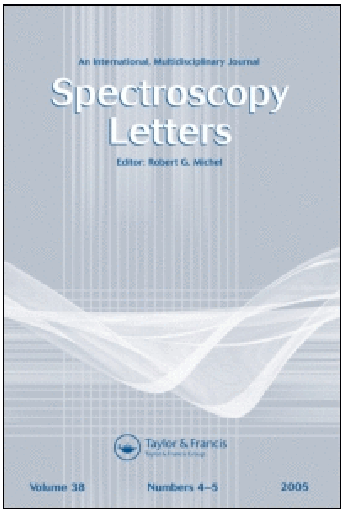

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Determination of Thallium by Atomic Absorption Spectrophotometry. II

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DETERMINATION OF THALLIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY. II*)

KEY WORDS: atomic absorption, thallium

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Summary. Besides the enhancing effect caused by some anions, the depressing effect by formate, acetate, propionate and vanadate ions on the AA-determination of thallium at a relatively low temperature is presented.

1. Introduction

In a previous paper[1] the determination of thallium by AAS was reported. It was found that various cations and anions have an enhancing effect on the absorption of thallium when use is made of a relatively cool flame, fed with propane and air. However, further experiments showed that the cation interference does not hold completely and that the interference, i.e. increasement in absorption, is rather due to anions than to cations. For instance, by comparing the absorption of thallium with interferent added as a sulphate and the corresponding quantity SO_4 added as H_2SO_4, it is seen that there will be no difference.

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*) Part I: Z. anal. Chem. 223, 17 (1966)

2. Instrumentation

The experimental conditions for the AA-determination of thallium are the same as described in the previous paper[1] and will be summarized as follows:

Light source	- hollow cathode lamp (ASL, Melbourne)
Lamp current	- 12 mA, stabilized with Stabilizer from the Hilger and Watts Atomic Absorption Attachement H 909
Spectrophotometer	- Zeiss PMQ II
Optics	- primary image of source in the flame, secondary image on the entrance slit of the monochromator
Chopper	- between source and flame, 50 Hz
Fuel gases	- air/propane, air 5,8 l/min, propane 0,41 l/min
Wavelength	- 276,8 nm
Slit width	- 0,2 mm

3. Depressing effects on the thallium absorption

It was found that formate, acetate, propionate and vanadate ions have a depressive effect on the thallium absorption. First, we shall consider the organic interference. From Table 1 it can be seen that formate, acetate and propionate ions diminish the absorption of thallium. An interesting feature is that the free acids have no depressing effect on the absorption. This difference in behaviour between the acid and the corresponding salt suggests that, while the acids are only slightly dissociated in solution, the depressing effect on the absorption is due to the *free* anions in solution. Further, it is interesting to remark that there will be seen hardly any effect with higher temperature flames ($t > 2200$ ^{0}C). The interfering influence of formate, acetate and propionate ions on the thallium absorption has been given in Figure 1. In this figure $|X^-|/|Tl^+|$, expressed in molar units, is plotted against the relative absorbance A/A_0; $|X^-|$ means the *free* ion concentration of the formate, acetate and propionate ion, respectively. From

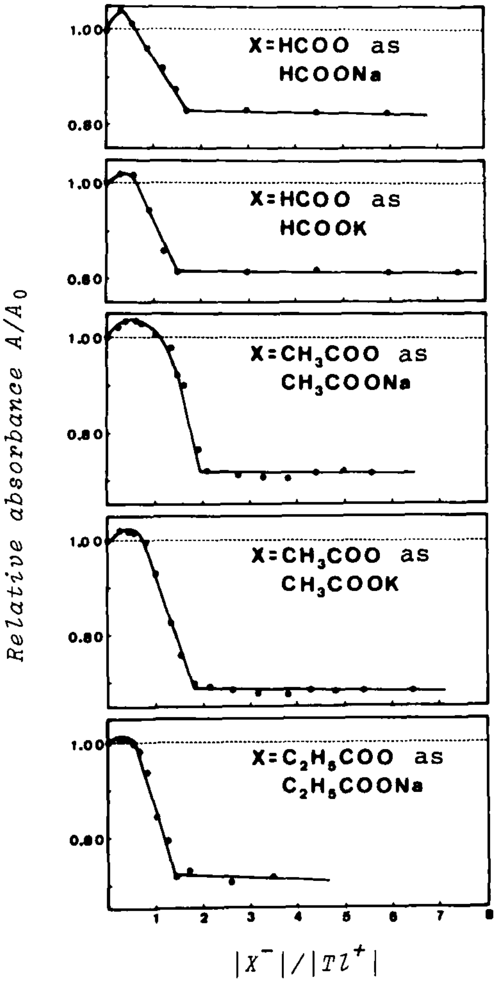

FIG. 1

The influence of formates, acetates and propionates on the absorption of thallium

TABLE 1

The influence of formate, acetate and propionate ions on the thallium absorption (Tl present as $TlNO_3$) in comparison with the influence of formic, acetic and propionic acid, respectively

A/A_0 = relative absorbance
A_0 = absorbance of thallium solution alone
A = absorbance of thallium solution plus interferent

Interferent	A/A_0		
	30 ppm Tl + 40 ppm interferent	30 ppm Tl + 100 ppm interferent	30 ppm Tl + 1000 ppm interferent
HCOO as HCOOK	0.87	0.87	0.87
HCOO as HCOOH	1.03	1.08	1.10
CH_3COO as CH_3COOK	0.72	0.74	0.90
CH_3COO as CH_3COOH	1.02	1.03	1.07
C_2H_5COO as C_2H_5COONa	0.79	0.77	0.81
C_2H_5COO as C_2H_5COOH	1.02	1.04	1.06

Figure 1 it is seen that the absorption is initially enhanced and then depressed. After a certain molar ratio $|X^-|/|Tl^+|$ there will be no further decreasing effect. In most cases the ratio $|X^-|/|Tl^+|$ varies between 1,1 and 2,0.

The influence of the measure height above the burner tip on the relative absorbance is demonstrated in Figure 2. It can be seen that the molar ratio $|X^-|/|Tl^+|$ remains constant, but the plateau is a function of the measure height. From this figure we can also see that this cannot be a temperature effect.

At last, the influence of the vanadate ion has been investigated. The absorbance of 30 ppm Tl (as $TlNO_3$) is decreased with 24, 93 and 93% by 10 ppm VO_3, 100 ppm VO_3 and 1000 ppm VO_3, respectively. Also with higher temperature flames the absorption is greatly decreased.

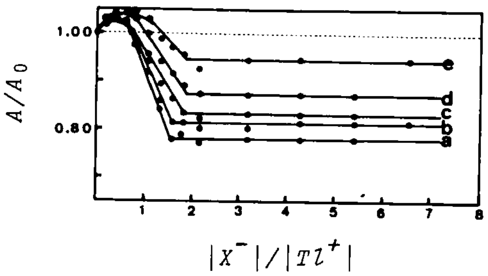

FIG. 2

The effect of the measure height above the burner tip on the relative absorbance A/A_0

$X = CH_3COO$ added as CH_3COOK

a = 0.8 cm above the burner, t = 1831 °C

b = 1.3 cm, t = 1854 °C

c = 1.8 cm, t = 1835 °C

d = 2.3 cm, t = 1822 °C

e = 2.8 cm, t = 1784 °C

4. Discussion

We have seen that thallous nitrate gives a higher absorbance than thallous acetate. From the observation that thallous acetate gives a lower absorbance than thallous nitrate the only conclusion which can be drawn is that thallous nitrate after crystallization as hydrate releases water molecules on heating and becomes the dehydrated nitrate, which volatilizes easier than the thallic oxide which is formed by decomposition of thallous acetate. Herewith it is assumed that the nitrate undergoes also some transformation into oxide.

A possible reaction scheme may be:

$$\rightarrow \underset{206^0C\ (g)}{TlNO_3} \text{ ....(1)}$$

$$\underset{(l)}{TlNO_3 . H_2O} \rightarrow \underset{(s)}{TlNO_3} \rightarrow$$

$$\rightarrow \underset{300^0C\ (s)}{Tl_2O_3} \text{ ....(2)}$$

$$\underset{(l)}{CH_3COOTl . H_2O} \rightarrow \underset{(s)}{CH_3COOTl} \rightarrow \underset{131^0C\ (s)}{Tl_2O_3} \text{ ....(3)}$$

It is seen that thallous nitrate which has a melting point of 206 °C shall evaporate for a part into the gaseous state with some decomposition. Thallous acetate, however, has a lower melting point of 130 °C and shall be totally transformed upon heating into oxide.

A further assumption has now to be made viz.: that the gaseous thallous nitrate dissociates easier than thallic oxide in the flame, an assumption which is strengthened by the fact that the difference in absorption is lost at higher temperatures. The maximum temperature of the flame is 1830 °C which is about the same temperature where decomposition of the oxide begins to start. At higher temperatures therefor thallic oxide can be easily decomposed.

The other organic interferents will behave in a similar way. The strong depression of the vanadate ion can be explained by the assumption that thallous vanadate is very difficult to volatilize, even at higher temperatures.

In this way it is also clear why the absorption of thallous acetate is a function of the measure height above the burner. We have assumed that there will be formed Tl_2O_3 and with increasing height above the burner the oxide has got more time to volatilize. The result is that the absorption is less decreased with increasing burner height.

We have now come to interpret the molar ratio $|X^-|/|Tl^+|$ at which no further depressing of the thallium absorption occurs. We must expect the forming of thallous formate, acetate or propionate in the flame with a molar ratio 1:1. However, with the volatilization process the dissociation equilibrium of the salts in the droplets will alter. This has the consequence that the found molar ratio is higher than would be expected.

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