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Publisher *Taylor & Francis*

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## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Trifluoroethylxanthate as an Analytical Reagent: AAS of Zinc, Antimony and Lead After Coprecipitation of Their Trifluoroethylxanthates onto Microcrystalline Naphthalene

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**To cite this Article** Hussain, M. F. , Katyal, M. , Puri, B. K. and Takagi, Y.(1990) 'Trifluoroethylxanthate as an Analytical Reagent: AAS of Zinc, Antimony and Lead After Coprecipitation of Their Trifluoroethylxanthates onto Microcrystalline Naphthalene', *International Journal of Environmental Analytical Chemistry*, 38: 4, 525 – 531

**To link to this Article:** DOI: 10.1080/03067319008026954

**URL:** <http://dx.doi.org/10.1080/03067319008026954>

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# TRIFLUOROETHYLXANTHATE AS AN ANALYTICAL REAGENT: AAS OF ZINC, ANTIMONY AND LEAD AFTER COPRECIPITATION OF THEIR TRIFLUOROETHYLXANTHATES ONTO MICROCRYSTALLINE NAPHTHALENE

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*(Received 8 April 1987; in final form 8 June 1989)*

A sensitive method has been developed for the direct atomic absorption spectrometric determination of zinc, antimony and lead after coprecipitation of their trifluoroethylxanthates onto microcrystalline naphthalene. The metal xanthates are quantitatively coprecipitated over the pH ranges: Zn, 5.9-8.4; Sb, 4.0-6.0 and Pb, 4.0-11.0. The solid mass consisting of the metal complex and naphthalene is dissolved in DMF. This solution is aspirated into an air-acetylene flame at 213.9, 217.6 and 217.0 nm for Zn, Sb and Pb, respectively. Beer's law is obeyed in the concentration range 2-50, 3-90 and 5-60 µg of Zn, Sb and Pb, respectively in 10 ml of the final DMF solution. RSDs are at the  $\pm$  (0.5-0.6)% level ( $n=10$ ). The concentration for 1% absorption is 0.019, 0.035 and 0.060 µg/ml for Zn, Sb and Pb, respectively. The method is suitable for the preconcentration of the metals from a larger volume of the aqueous phase, and has been employed for their determination in standard reference materials. It may be employed for the simultaneous determination of Zn, Pb and Sb in a solution by pH control.

**KEY WORDS:** Trifluoroethylxanthate, naphthalene, atomic absorption spectrometry, determination of zinc, antimony and lead, analysis of standard reference materials.

## INTRODUCTION

Zinc and lead are found quite frequently in trace amounts in alloys, beverages, biological samples, foods and plant materials. Antimony is present in trace amounts in metals like zinc and lead. Numerous complexing agents for the determination of these metals have been reported in the literature. Some of the reagents which have recently been utilized for their determination are: 2,2'-

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dipyridyl-2-quinolyldiazone,<sup>1</sup> methylthymol blue,<sup>2</sup> 1-(2-pyridylazo)-2-naphthol,<sup>3</sup> basic triphenylmethane dyes<sup>4</sup> and heterocyclic amines sulfophthalein dyes<sup>5</sup> for zinc, brilliant green,<sup>6</sup> crystal violet,<sup>7</sup> 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol,<sup>8</sup> 4,5-dibromophenylfluorone<sup>9</sup> 2-(3,5-di bromopyridylazo)-5-dimethylaminophenol<sup>10</sup> for antimony and N-p-chlorophenyl-benzohydroxamic acid<sup>11</sup> and mexityloxide<sup>12</sup> for lead. Preliminary observations have revealed that these metal trifluoroethylxanthates are colourless and partially soluble in organic solvents, but can readily be coprecipitated onto microcrystalline naphthalene. Metal complex-naphthalene mixture can be dissolved in solvents like dimethylformamide (DMF) or acetonitrile. Therefore, in the present communication conditions have been developed for the trace determination of these metals by direct atomic absorption spectrometry (AAS) after coprecipitation of their trifluoroethylxanthates onto microcrystalline naphthalene and subsequent dissolution in DMF. The method is suitable for the preconcentration of the metal ions from a larger volume of the aqueous phase and, consequently is much more sensitive than the direct AAS method for these metals. It has been applied for the determination of zinc, antimony and lead in standard reference materials. The metal ions can be determined simultaneously in a solution by pH control.

## EXPERIMENTAL

### *Reagents*

Potassium trifluoroethylxanthate was prepared by the method of DeWitt and Roper,<sup>13</sup> 0.2 g of the reagent was dissolved in 2 ml DMF + 98 ml of water.

Solutions of zinc sulphate, antimony trichloride (in 8% HCl) and lead nitrate were prepared from their analytical-grade materials and standardized.<sup>14</sup> Buffer solutions were prepared from 1 M acetic acid and 1 M ammonium acetate for pH 3–6, and 1 M aqueous ammonia and 1 M ammonium acetate for pH 8–11. The naphthalene solution was prepared by dissolving 20 g naphthalene in 100 ml of acetone. Solutions of interfering ions were prepared in distilled water from analytical grade salts.

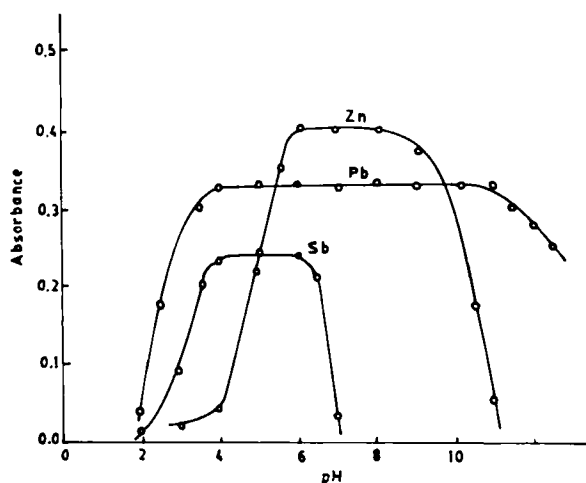
### *Equipment*

All absorbances were measured with a Pye Unicam SP-191 atomic absorption spectrometer with air acetylene burner head. Zinc, antimony and lead hollow cathode lamps from Pye Unicam were used. The pH measurements were carried out with an Elico pH meter with a glass electrode.

## RESULTS AND DISCUSSION

### *General Procedure*

To aliquots of the metal ion solutions were added 2 ml of reagent solution. The pH was adjusted to 5.9–8.4, 4.0–6.0 and 4.0–11.0 with aqueous ammonia and



**Figure 1** Effect of pH on coprecipitation. Wavelength: Zn, 213.9 nm; Sb, 217.6 nm; Pb, 217 nm. Amount analyzed: Zn, 17.6  $\mu\text{g}$ ; Sb, 19.7  $\mu\text{g}$ ; Pb, 46.0  $\mu\text{g}$ . Xanthate solution: 2.0 ml; 20% naphthalene-acetone solution: 2.0 ml. Preference: reagent blank. For other details, see text.

perchloric acid for zinc, antimony and lead, respectively. Alternatively, the pH could be adjusted to 8.0, 5.0 and 10.0 for zinc, antimony and lead, respectively with 2 ml of the buffer solutions. The solution was transferred to a 100 ml stoppered Erlenmeyer flask and enough 1 M potassium nitrate added to give an overall concentration of more than 0.1 M in 30 ml of the final solution. The solution was shaken thoroughly and allowed to stand for 5 min. Coprecipitation was carried out with 2 ml of naphthalene solution by shaking the content of the flask vigorously for 1–2 min at room temperature. The solid mass consisting of metal complex and naphthalene was separated by filtration, washed with distilled water and dissolved in DMF in a 10 ml standard flask. The solution was aspirated into air-acetylene flame at 213.9, 217.6 and 217.0 nm for zinc, antimony and lead, respectively.

### *Effect of pH*

Coprecipitations were carried out at different pH values keeping other conditions constant. The absorbance remained constant in the pH ranges 5.9–8.4, 4.0–6.0 and 4.0–11.0 (Fig. 1) for zinc, antimony and lead, respectively. Addition of 1–5 ml of buffers of pH 8.0 for zinc, 5.0 for antimony and 10.0 for lead caused virtually no variation in the absorbance. Subsequent studies were carried out with 2 ml of the buffer solution.

### *Reaction Conditions*

The following conditions were examined by taking 17.6, 19.7 and 46.0  $\mu\text{g}$  of zinc, antimony and lead, respectively.

Coprecipitations were carried out at a fixed pH in each case and with varying

amounts of the reagent. Although the coprecipitation was quantitative in each case when slightly more than the stoichiometric amount of the reagent was used, in all cases 2 ml of the reagent solution were used for safety. Various electrolytes such as sodium nitrate, potassium nitrate and sodium perchlorate (0.01–0.5 M) were added. The coprecipitation was found to be quantitative if the electrolyte concentration was more than 0.01 M. Hence, 0.1 M potassium nitrate was used throughout the present work.

A minimum standing time of 5 min at room temperature is recommended, although only 2 min is needed for the complete complex formation. The coprecipitation is very rapid, being practically complete in less than 30 sec, and a shaking time of 1–2 min gives an ample safety margin. A minimum of 0.5 ml of naphthalene solution in acetone is required for complete coprecipitation; the use of 2 ml is recommended.

Since only a small amount of organic phase (0.4 g) is used, the volume of the aqueous phase is important. The coprecipitation is maximum and constant if the aqueous phase volume is less than 100 ml; it is best kept to 30–40 ml.

#### *Beer's Law and Sensitivity*

Under the optimum conditions developed above, calibration curves were constructed at 213.9, 217.6 and 217.0 nm against reagent blank for zinc, antimony and lead, respectively. Beer's law was obeyed in the concentration range 2–50, 3–90 and 5–60  $\mu\text{g}$  of zinc, antimony and lead, respectively, in 10 ml of the final DMF solution. Ten replicate determinations of the sample solutions containing 17.6  $\mu\text{g}$  of zinc, 19.7  $\mu\text{g}$  of antimony and 46.0  $\mu\text{g}$  of lead gave mean absorbances of 0.400, 0.240 and 0.330 with RSDs of  $\pm 0.64$ ,  $\pm 0.52$  and  $\pm 0.49\%$ , respectively. The concentrations for 1% absorption were found to be 0.019, 0.035 and 0.060  $\mu\text{g}/\text{ml}$  for zinc, antimony and lead, respectively, while for the direct AAS determination of these metals from the aqueous solutions were found to be 0.050, 0.100 and 0.500  $\mu\text{g}/\text{ml}$  for zinc, antimony and lead, respectively. Naturally, the method is more sensitive, and the sensitivity can be further improved by carrying out the coprecipitation of these metals from 100 ml of the aqueous phase instead of 30 ml as suggested in the general procedure.

#### *Effect of Diverse Ions*

The effect of various salts of anions on the coprecipitation and, subsequently, on the AAS determination of 17.6  $\mu\text{g}$  of zinc, 19.7  $\mu\text{g}$  of antimony and 46.0  $\mu\text{g}$  of lead was studied. Salt of anions such as sodium fluoride, sodium nitrite, sodium nitrate, sodium phosphate, sodium carbonate, potassium thiocyanate, sodium acetate, sodium oxalate, sodium citrate and ammonium tartrate could be tolerated up to 100 mg in all cases. Potassium chloride, potassium bromide, potassium iodide and sodium sulphate interfered in the determination of lead only, while there was no interference from these salts in the determination of zinc and antimony up to 100 mg each. Relatively low amounts (10 mg) could be tolerated in the determi-

nation of lead. Coprecipitation was not possible in the presence of EDTA, probably due to the higher formation constant of the metal-EDTA complexes compared to the xanthates.

The metal ions Al(III), V(V), Mo(VI), Bi(III), Cd(II), Cr(III), Co(II), In(III), Ir(III), Fe(III), Mn(II), Hg(II), Ni(II), Nb(V), Os(VIII), Pd(II), Pt(IV), Te(IV), Rh(III), Se(IV), Ru(III), Ag(I), As(III), W(VI), Tl(I), Th(IV), U(VI), Mg(II), and Zr(II) can be tolerated up to 20-fold excess in all cases. The interference of Cu(II) in the determination of lead and antimony can be eliminated with 10 ml of 5% sodium cyanide solution during adsorption.<sup>15</sup> In the determination of zinc, copper can be removed from the solution by pre-extracting it as its diethyldithiocarbamate into chloroform.<sup>16</sup> There is no interference of zinc and antimony in the determination of lead if the coprecipitation is carried out at pH 10. Antimony does not interfere in the determination of zinc at pH 8. The interference of zinc and lead in the determination of antimony can be eliminated by coprecipitating their xanthates at pH 8; in the filtrate antimony is then determined by the general procedure. In the determination of zinc, the interference of lead is eliminated by first coprecipitating lead at pH 10 and, then, zinc can be determined in the filtrate by the general procedure. Thus a simultaneous method can be developed for the determination of zinc, antimony and lead simply by the control of pH values.

#### *Determination of Zn, Sb and Pb in Standard Reference Materials*

A 0.1–5.0 g sample of the standard reference material was decomposed with 10–50 ml of hydrochloric acid (1+1) and 2–10 ml of concentrated nitric acid. It was heated in a water-bath till the sample dissolved and the volume of the solution reduced to about 10 ml (in case of pond sediments the solution was transferred to a PVC beaker and treated with about 5 ml of hydrofluoric acid for dissolving the sample completely). After cooling, concentrated hydrochloric acid (5 ml) and approx. 20 ml of distilled water were added to dilute the solution. It was filtered (if needed) and filtrate was diluted to 100 ml in a standard flask. The interfering metal ions were masked as described in the text and the desired metal ion was determined by the general procedure. The results which are presented in Table 1, show the practicality of the present method.

**Table 1** Analyses of Standard references materials for Zinc, Antimony and Lead

Sample	Certified Composition (%)	Metals determined by the present method (%) <sup>a</sup>		
		Zinc	Antimony	Lead
N.B.S. SRM-85 Sb Al alloy	Zn: 0.03, Pb: 0.021 Ti: 0.022, Ni: 0.083 Si: 0.018, Cr: 0.211 Mg: 1.49, Cu: 3.99 V: 0.006, Ga: 0.019 Fe: 0.24, Mn: 0.61	0.032 ± 0.0005	—	0.02 ± 0.004
N.B.S. SRM-171 Mg alloy	Zn: 1.05, Pb: 0.0033 Mn: 0.45, Ni: 0.0009 Cu: 0.0112, Si: 0.0118 Al: 2.98, Fe: 0.0018	1.07 ± 0.03	—	0.0038 ± 0.0005
SRM, 54d Tin-base Bearing metal Alloy	Sb: 7.04, Pb: 0.62 Sn: 88.57, Cu: 3.62 As: 0.0088, Bi: 0.044 Fe: 0.027, Ag: 0.003 Ni: 0.002	—	7.25 ± 0.15	0.64 ± 0.02
NKK 1021 Aluminium Alloy	Zn: 1.76, Pb: 0.18 Sb: 0.01, Ni: 0.14 Fe: 0.99, Ti: 0.04 Sn: 0.10, Mn: 0.20 Si: 3.56, Mg: 0.29 Cr: 0.03, V: 0.007 Zr: 0.01, Bi: 0.01 Ca: 0.004	1.82 ± 0.05	0.012 ± 0.001	0.185 ± 0.007
SRM 127b Lead-base Alloy	Sb: 0.43, Bi: 0.06 Ag: 0.01, Sn: 39.9 As: 0.01, Cu: 0.11	—	0.41 ± 0.02	—
SRM, 94c Zinc alloy	Pb: 0.006, Cd: 0.002 Sn: 0.006, Ni: 0.006 Mn: 0.014, Fe: 0.018 Mg: 0.042, Cu: 1.01 Al: 4.07	—	—	0.0062 ± 0.0003
NIES No. 2 Pond sediment	Zn: 0.035, Pb: 0.011 Al: 10.6, Fe: 6.55 Ca: 0.81, K: 0.68 Na: 0.57, Cr: 0.0075 Ni: 0.004, Co: 0.0027 As: 0.00012, Cd, 0.00008 Cu: 0.021	0.034 ± 0.001	—	0.010 ± 0.001

<sup>a</sup>Average ± standard deviation (mean of five determinations).

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