

## Complexation between Antimony and *o*-Chlorophenylfluorone and its Application to Determination of Antimony in Wastewater

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**Abstract.** The formation of a chelate complex of antimony(III) with *o*-chlorophenylfluorone (CPF) was used for the spectrophotometric determination of antimony. The spectral correction technique was applied to characterize the complexation and the determination of Sb<sup>III</sup>. Results have shown that complex Sb(CPF)<sub>2</sub>H<sub>2</sub>O was formed and its stepwise stability constants were determined to be  $\log K_1=6.44$  and  $\log K_2=5.81$ . The molar absorptivities of the complex at pH=4.5 and at 540 nm were  $\varepsilon_1=1.38 \times 10^4$  and  $\varepsilon_2=3.46 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The method is characterised by selectivity in the presence of the mixture of thiourea, triethanolamine and ethylenebis(oxyethylenitrilo)-tetraacetic acid. The limit of detection is  $0.03 \mu\text{g cm}^{-3}$  of Sb<sup>III</sup>. Analysis of wastewater samples was performed with satisfactory results.

**Keywords:** spectral correction technique, *o*-chlorophenylfluorone, spectrophotometry, determination of antimony, wastewater

### INTRODUCTION

Antimony is rare in nature and unpolluted water typically contains less than  $1 \text{ ng cm}^{-3}$  of Sb. It often exists in wastewater discharged from metallurgical, ore dressing, and electroplating, printing, leather-manufacturing, pharmaceutical factories. Sb belongs to the group of non-essential elements and its toxicity is comparable to arsenic and bismuth. The United States Environmental Protection Agency (EPA) lists Sb and its compounds as the priority pollutants. Most common current methods for the determination of Sb<sup>III</sup> species in aqueous solution include hydride generation atomic absorption spectroscopy,<sup>1</sup> GC-MS,<sup>2</sup> differential pulse stripping voltammetry<sup>3,4</sup> etc. Only a few spectrophotometric methods are applied to detection of antimony, e.g., some ordinary spectrophotometric methods,<sup>5</sup> kinetic spectrophotometric methods<sup>6,7</sup> and first-derivative spectrophotometric method.<sup>8</sup> These methods are also used along with some other technologies, e.g., partial least squares method,<sup>9</sup> flow injection,<sup>10</sup> and solvent extraction.<sup>11</sup> Compared to other methods, the spectrophotometric method has its advantages, such as low cost, simple operation, easy spread and wide application. Up to now, it has been studied extensively, particularly in the developing countries.

The purpose of the present work is to investigate the complexation between antimony(III) and *o*-chloro-

phenylfluorone (CPF) by the spectral correction technique, which has greatly improved determination of metal ions instead of ordinary spectrophotometry.<sup>12, 13</sup> The Sb<sup>III</sup>-CPF complex was used to detect antimony concentration in wastewater and the effect of other metal ions on Sb<sup>III</sup> determination was studied.

### EXPERIMENTAL

#### Apparatus and Reagents

A double-beam spectrophotometer, Model Lambda-25 (Perkin-Elmer, USA), with UV WinLab software (Version 2.85.04), was used for absorption measurements. The solution pH was measured with a pH meter Model PHS-25 (Shanghai Precise Science Instruments, China).

Antimony(III) stock solution ( $1.000 \text{ mg cm}^{-3}$ ) was prepared by dissolving 1.000 g of high-purity antimony (> 99.9 %, A. R., Shanghai Chemicals, China) in  $25 \text{ cm}^3$  of sulfuric acid (A. R., Shanghai Chemicals, China) and heating for dissolution, and the volume was made up to  $1000 \text{ cm}^3$  with deionized water. Working solutions were obtained by suitable dilution of the stock solution with deionized water.

CPF ( $1.00 \mu\text{mol cm}^{-3}$ ) was used. The solution was prepared as described earlier.<sup>14</sup>

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Surfactant solutions (all with surfactant mass fraction,  $w=1\%$ ) were prepared: Triton X-100, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl benzene sulfonate (SDBS) (Shanghai Chemical Regents Co., China Medicals). The masking reagent was prepared by mixing 5 g of thiourea, 4 cm<sup>3</sup> of triethanolamine (A. R., Zhengzhou Chemicals, China) and 4 g of ethylenebis(oxyethylenitrilo)-tetraacetic acid (EGTA, A. R., Fudan University, China) and diluting it to 200 cm<sup>3</sup> with deionized water.

### Complex Characterization

20.0 μg of Sb<sup>III</sup> was placed in a 25-cm<sup>3</sup> volumetric flask. 2.5 cm<sup>3</sup> of acetate buffer solution, pH=4.5,<sup>15</sup> 1 cm<sup>3</sup> of a surfactant solution and a known volume of 1.00 μmol cm<sup>-3</sup> CPF were added. The volume was made up to the mark with water and the solution was mixed well. After 10 min, solution absorbances were measured at 430 and 540 nm against a reagent blank, respectively. The constants were calculated as described earlier.<sup>16</sup>

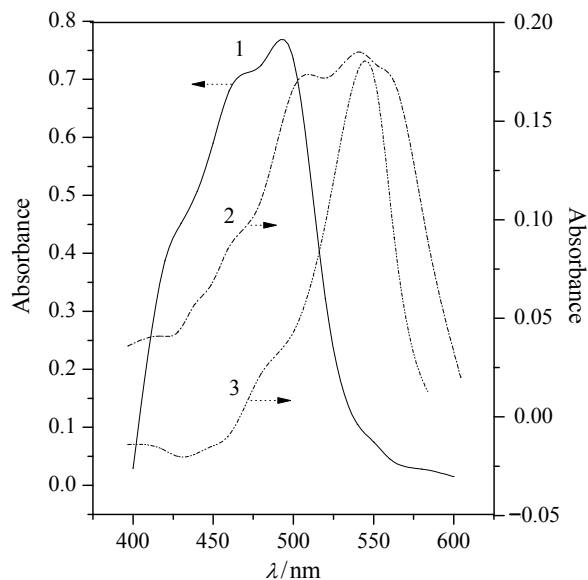
**Determination of Sb<sup>III</sup>.**<sup>17</sup> 50 cm<sup>3</sup> of a wastewater sample solution was mixed with 10 cm<sup>3</sup> of concentrated sulfuric acid. The mixture was heated until evaporated to the volume of about 10 cm<sup>3</sup>, then neutralized with 10% (w) NaOH and filtered. Filtrate solution was diluted to 50 cm<sup>3</sup>. Suitable aliquots of sample solution were analyzed for antimony as describe above.

## RESULTS AND DISCUSSION

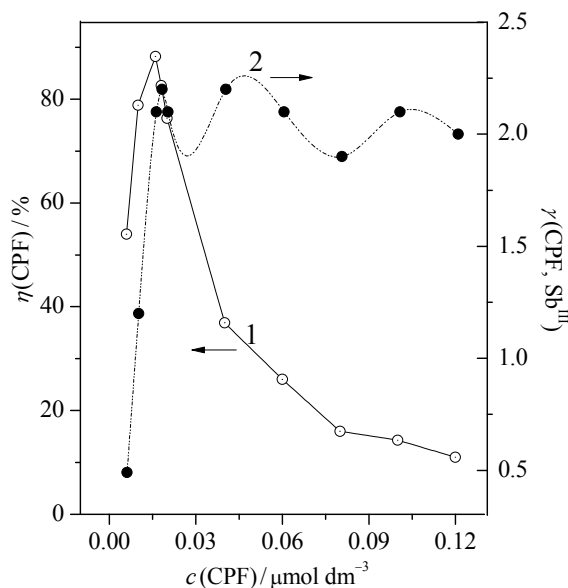
Absorption spectra of CPF and its Sb<sup>III</sup>-CPF complex solutions recorded against water have their maxima at 496 and 540 nm, in case of pH=4.5, in the presence of Triton X-100 (Figure 1, curves 1 and 2). However, in the absorption spectra of the Sb<sup>III</sup>-CPF complex recorded against a reagent blank the valley is located at 430 nm (Figure 1, curve 3). Both 430 and 540 nm were therefore selected as work wavelengths so as to reach a maximal peak-valley interval.

The influence of CPF addition on the solutions containing 0.80 μg cm<sup>-3</sup> Sb<sup>III</sup> was examined. Absorbances remain maximally constant when CPF concentration is higher than 0.016 μmol cm<sup>-3</sup>. The effective fraction ( $\eta$ ) of CPF and the composition ratio ( $\gamma$ ) of CPF to Sb<sup>III</sup> calculated according to literature<sup>16</sup> are shown in Figure 2. From curve 1,  $\eta$  increases from 58% up to 90% with increasing the CPF concentration from 0.006 to 0.016 μmol cm<sup>-3</sup> and then decreases after further increasing it above 0.016 μmol cm<sup>-3</sup>.  $\gamma$  almost remains a constant maximum at 2 when CPF concentration is higher than 0.016 μmol cm<sup>-3</sup>. As a result, the Sb(CPF)<sub>2</sub>H<sub>2</sub>O complex can be formed.

By varying the solution pH between 3.0 and 7.5,



**Figure 1.** Absorption spectra of the CPF and Sb<sup>III</sup>-CPF complex solutions at pH=4.5 in the presence of Triton X-100 ( $w=0.04\%$ ): (1) CPF, 0.040 μmol cm<sup>-3</sup>, (2) Sb<sup>III</sup>, 16 μg cm<sup>-3</sup>; CPF, 0.010 μmol cm<sup>-3</sup>, (3) Sb<sup>III</sup>, 0.80 μg cm<sup>-3</sup>; CPF, 0.040 μmol cm<sup>-3</sup>. Both 1 and 2 against water and 3 against a reagent blank.



**Figure 2.** Variations of  $\eta$  and  $\gamma$  of the solutions initially containing 0.80 μg cm<sup>-3</sup> Sb<sup>III</sup> and CPF between 0.006 and 0.120 μmol cm<sup>-3</sup>.

the peak-valley absorbance interval remains a constant maximum between pH=3 and 5, As a result, pH=4.5 acetate buffer solution was added in this work.

The presence of surfactants might provide a higher complexation ability with a catalytic field.<sup>18</sup> Three types of surfactants: Triton X-100 as non-ionic surfactant, CTAB as cationic surfactant and SDBS as anion surfactant were

added and their effects on the interval between peak and valley absorptions of the complex solution were measured. Triton X-100 gives the longest interval. The light-absorption of Sb<sup>III</sup>-CPF solution approaches a maximum while more than 0.5 cm<sup>3</sup> of 1% (w) Triton X-100 is present. Hence, 1.0 cm<sup>3</sup> of 1% Triton X-100 was added in this work.

The effect of time indicated that the reaction was complete in 5 min in the presence of Triton X-100 and the absorbance of the solution remained almost constant for at least 2 h.

The stepwise stability constant ( $K_n$ ) and the stepwise absorptivity ( $\varepsilon_n$ ) of the complex were calculated.<sup>16</sup> Two solutions were prepared: one contained 0.80  $\mu\text{g cm}^{-3}$  of Sb<sup>III</sup> and 0.006  $\mu\text{mol cm}^{-3}$  of CPF and the other 0.80  $\mu\text{g cm}^{-3}$  of Sb<sup>III</sup> and 0.012  $\mu\text{mol cm}^{-3}$  of CPF. Results are given as follows:  $\log K_1 = 6.44$ ,  $\log K_2 = 5.81$ ,  $\varepsilon_1 = 1.38 \times 10^4$  and  $\varepsilon_2 = 3.46 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 540 nm at 15 °C in the medium of ionic strength  $I_c = 0.01 \text{ mol dm}^{-3}$ . Thus,  $\log K = 12.25$ . From  $\varepsilon_2$ , the complex reaction is sensitive.

A series of standard solutions containing Sb<sup>III</sup> (between 0 and 40.0  $\mu\text{g}$ ) were prepared and the absorbance of each solution was measured. The regression equations at 540 nm are:  $A_c = 0.0169x - 0.006$  ( $R = 0.9996$ ) and  $\Delta A = 0.0150x - 0.006$  ( $R = 0.9957$ ), where  $x$  is the Sb concentration expressed in  $\mu\text{g cm}^{-3}$ . From the  $R$  values and the line slopes, both the accuracy and sensitivity of the spectral correction technique are better than those of ordinary spectrophotometry.

Six replicated determinations of a standard solution containing 5.00  $\mu\text{g}$  of Sb<sup>III</sup> were carried out. The mean  $\pm$  standard deviation and relative standard deviation were  $4.98 \pm 0.11 \mu\text{g}$ , and 2.2% by the proposed method. However, they were  $4.81 \pm 0.35 \mu\text{g}$ , and 7.3% by the single wavelength spectrophotometry. The limit of detection (LOD), defined as the average of 10 replicated blanks plus 3 times of the standard deviation of the blank,<sup>19</sup> was calculated to be  $0.03 \mu\text{g cm}^{-3} \text{ Sb}^{\text{III}}$ .

Once the masking reagent as a mixture of thiourea, triethanolamine and EGTA was added, none of the following ions will affect the direct determination of 10.0  $\mu\text{g}$  of Sb<sup>III</sup> (<5% error): 1000  $\mu\text{g}$  of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>II</sup>, Mg<sup>II</sup>, Ba<sup>II</sup>, Cu<sup>II</sup>; 300  $\mu\text{g}$  of Hg<sup>II</sup>, Cd<sup>II</sup>; 150  $\mu\text{g}$  of La<sup>II</sup>, Au<sup>III</sup>; 60  $\mu\text{g}$  of Ni<sup>II</sup>, Co<sup>II</sup>, Sn<sup>II</sup>, Ag<sup>I</sup>, Pt<sup>IV</sup>, Cr<sup>III</sup>, Zn<sup>II</sup>; 20  $\mu\text{g}$  of Mn<sup>II</sup>, Al<sup>III</sup> and 10  $\mu\text{g}$  of V<sup>V</sup>, Ti<sup>IV</sup>, Fe<sup>II</sup>, Ge<sup>IV</sup>.

### Sample Analysis

To test the method, two wastewater samples were analyzed. They were obtained from a metallurgic plant (sample #1) and an electroplating workshop (sample #2). Before determination, every sample must be pre-treated according to the mentioned procedures. Analysis results of (Table 1) were in good agreement with those obtained by atomic fluorescence spectrophotometry (AFS). The recommended method is accurate and feasible in the section of determination of antimony in wastewater.

### CONCLUSION

Formation of the Sb<sup>III</sup>-CPF complex has been studied by the spectral correction technique. The recommended method is simple, sensitive and selective for the determination of Sb<sup>III</sup>. The advantage of the present procedure is that it does not require many reagents and has a low RSD value. The relative standard deviation for six replicate measurements of 5.00  $\mu\text{g cm}^{-3}$  of antimony(III) was 2.2%, whereas single wavelength spectrophotometry gave a RSD value 7.3%. The method has been applied to determine antimony in wastewater samples with acceptable results.

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**Table 1.** Determination of antimony in wastewater. Conditions:  $c_{\text{CPF}} = 0.040 \mu\text{mol dm}^{-3}$ , pH = 4.5

| Sample | $\gamma(\text{Sb})^{(a)}/\mu\text{g cm}^{-3}$ |                            | RSD/%             | Recovery/% |
|--------|---|----------------------------|-------------------|------------|
|        | Added   | Found                      |                   |            |
|        |   | Prop. meth. <sup>(b)</sup> |                   |            |
| #1     | 0   | 0.628 $\pm$ 0.04           | 0.622 $\pm$ 0.032 | 6.4        |
|        | 1.25  | 1.88 $\pm$ 0.03            | 1.91 $\pm$ 0.04   | 1.59       |
| #2     | 0   | 1.24 $\pm$ 0.03            | 1.12 $\pm$ 0.04   | 2.4        |
|        | 1.25  | 2.56 $\pm$ 0.04            | 2.44 $\pm$ 0.05   | 1.56       |

<sup>(a)</sup> Average of four determinations

<sup>(b)</sup> Proposed method

<sup>(c)</sup> Atomic fluorescence spectrometry

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## SAŽETAK

## Kompleks antimonya s *o*-klorofenilfluoronom i njegova primjena za određivanje antimonya u otpadnim vodama

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Formiranje kelatnog kompleksa između antimonya(III) i *o*-klorofenilfluorona (CPF) upotrebjeno je za spektrofotometrijsko određivanje antimonya, pri čemu je korištena tehnika korekcije spektara. Rezultati su pokazali da nastaje kompleks sastava  $\text{Sb}(\text{CPF})_2\text{H}_2\text{O}$  čije su sukcesivne konstante stabilnosti iznosile  $\log K_1=6,44$  i  $\log K_2=5,81$ , a molarne apsorbivnosti  $\varepsilon_1=1,38 \times 10^4$  i  $\varepsilon_2=3,46 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , pri 540 nm i pH=4,5. Metoda je selektivna u prisutnosti smjese tiouree, trietanolamina i etilenbis(oksietilennitrilo)-tetraoctene kiseline. Granica detekcije za  $\text{Sb}^{\text{III}}$  je iznosila  $0,03 \mu\text{g cm}^{-3}$ . Analizom uzoraka otpadnih voda dobiveni su zadovoljavajući rezultati.