Comparative Study of Leuco Dyes as Reagents for Spectrophotometric Determination of Arsenic (Ⅲ)

Minori Kamaya[1*], Yusuke Ito[1], Yuki Otomura[1] and Elena Ginatullina[2]

[1] Kogakuin University, 2665-1, Nakano-machi
Hachioji-city, Tokyo, Japan

[2] Institute of Sanitary, Hygiene and Professional diseases
325 Oltyntepa, Tashkent, Uzbekistan

[*]*Corresponding author's email: bt74290 [AT] ns.kogakuin.ac.jp*

ABSTRACT— ***In this paper spectrophotometric determination arsenic (III) is described. The method is based on the two step reaction. First step is arsenic (Ⅲ) and iodate reaction in the acid medium of pH=1.1. In this step, iodine is liberated proportionally according to the amounts of arsenic (Ⅲ). Next step is the reaction of liberated iodine with leuco dyes in pH= 4-5. In this work, the leuco dyes was comparatively studied. The employed leuco dyes are malachite green (LMG), leuco crystal violet (LCV) and leuco berberin blue Ⅰ (LBB). The oxidized leuco dyes was determined by spectrophotometry. Beer's law is obeyed in the range of 0.1-0.1μg mL^{-1} as arsenic. The molar coefficient for arsenic (Ⅲ) was around 4×10^4 l mol^{-1} cm^{-1} with each leuco dyes. In these leuco dyes, LBB was suitable as reagent because not influenced temperature, concentration of iodate and LBB, and rapid reaction time.***

Keywords— arsenic(Ⅲ), leuco dyes, iodine, spectrophotometry

1. INTRODUCTION

An arsenic contamination in natural water is becoming a serious environmental problem. Arsenic occurs naturally in the earth crust in an inorganic trivalent or pentavalent form. It is appreciably recognized that trivalent arsenics are more toxic than pentavalent [1]. The determination of arsenic is a critical importance in protecting the population from the health hazards in poses [2].

The various analytical techniques are available for determination of arsenic by spectrophotometry [3], cathodic stripping voltammetry [4], anoidic stripping voltammetry [5], hydride generation atomic absorption spectrometry [6], ion chromatography and coupled plasma mass spectrometry [7], neutron activation analysis [8], potentiometry [9], hydride generation atomic fluorescence spectroscopy [10], and electrothermal atomic absorption spectrometry [11]. Among these methods, the spectrophotometric methods are widely used because of the low cost performance. Spectrophotometric methods for determination of arsenic **(Ⅲ)** are investigated with many reagents such as ammonium-hexamethylenedithiocarbamate [12], 2,4-dihydroxy benzophenone-2-amino thiophenol [13], azure B [14], ammonium pyrrolidine dithiocarbamate [15], Toluidine blue or Safranine O [16], leuco malachite green [17], and Rhodamine B [18].

As for these spectrophotometric methods, the leuco malachite green method is simply performed without using the solvent extraction [17]. The method is based on the reaction of arsenic (Ⅲ) with potassium iodate in acid medium to liberate iodine. The liberated iodine oxidizes the leuco malachite green (LMG) and color developing occurred by oxidation of LMG. Other leuco dye of LCV was also studied [19]. However, the sensitivity for arsenic is not coincided with the expected value calculated from chemical reactions. For this reason, it is need to test the comparison of leuco malachite green and leuco crystal violet. Moreover, in this paper, we have compared other leuco dye of LBB, which have not ever reported.

2. EXPERIMENTALS

2.1. Reagents

A working standard of arsenic **(Ⅲ)** solution was prepared by accurate dilution of 1000mg/L of standard arsenic solution (Wako Pure Chemical Industries, Co. Ltd) with water. Leuco dyes from Sigma Aldrich Co Ltd were dissolved with 0.3% (v/v) aqueous solution of phosphoric acid because of their solubility into the water is poor. Other chemicals were used on the analytical grade.

2.2. Instruments

Spectrophotometric measurements were carried out with a Shimadzu UV-1800 spectrophotometer using the 1 cm cells. A pH measurement was carried out with a TOA pH meter model HM-3uV.

2.3. Reaction mechanism

In acid medium arsenic (Ⅲ) react with iodate and liberates iodine. Next, the liberated iodine oxidizes leuco dyes. The reactions are carried out with following steps:

Step 1

$5AsO_3^{3-} + 2IO_3^- + 2\,H^+ \rightarrow 5AsO_4^{3-} + I_2 + H_2O$ (around pH1)

Step 2

I_2 + 2 leuco dyes $\rightarrow$2 I^- + 2 oxidized dye (around pH 4.5).

From these reactions, one mole of As (III) produces 0.4 moles of dyes. The molar coefficients of these dyes are near 1×10^5 l mol^{-1} cm^{-1} and the sensitivity was expected to be around 4×10^4 l mol^{-1} cm^{-1}. However, Agrawal et al [19] showed molar coefficient for arsenic as 1.49×10^6 l mol^{-1} cm^{-1}. The sensitivity obtained is very high and not explained by this reaction.

2.4. Optimal procedures

The 4mL aliquots of the standard solution containing from 2 to10 µg of arsenic (III) were taken in the 10 mL series of measuring flasks. The 1ml of 1% (w/v) KIO_3 and 0.5 mL of 1 mol L^{-1} HCl were added to the flasks and the reaction mixtures were standing for 2 min. Then, the 2 mL of buffer solutions (LMG and LCV with pH=4.2 and LBB with pH=5.0), and 0.5 mL of 0.05% leuco dyes are added and diluted to the mark with water. After 5 min, absorbance of the developed color solution using LMG, LCV and LBB are measured at 617 nm, at 590 nm, at 625 nm respectively.

3. RESULT AND DISCUSSION

3.1. Effect of pH

The formation and stability of the developed color are depends on the pH at the reaction of leuco dyes and iodine. The preparation and effect of pH on leuco dyes and iodine was studied by adding of hydrochloric acid solution to sodium acetate solution. It was found that the optimum value of pH for LMG and LCV was pH 4.2 and for LBB was pH 5.0 respectively (Fig.1). The blank values of the LMG and LCV increased when the pH was more high than pH 4, however, in the case of LBB, the blank value was not increased.

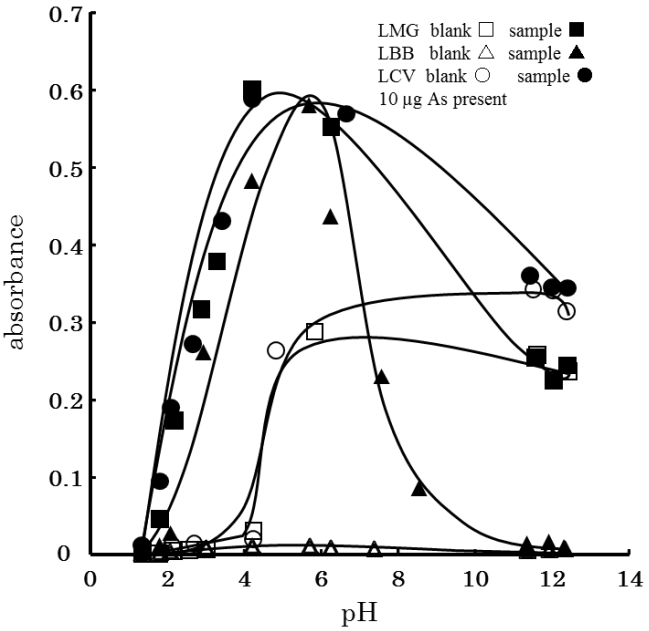

Figure 1: Effect of pH

3.2. Effect of reaction time of iodine and leuco dyes

The reaction rate of iodate and arsenite is very rapid only two second. The activation energy was also investigated using sulfuric acid, perchloric acid, and hydrochloric acid. The smaller value with hydrochloric acid can be attributed to the catalytic effect of chloride on the reaction rate [20]. For these reason, the reaction time with iodine and leuco dyes was investigated (Fig.2); as can be seen from Fig.2, the absorbance of blank using LMG was gradually increased. However, LCV and LBB dyes dose not increased. The absorbance was rapidly achieved constant values when LBB was used and the blank value was lowest in these leuco dyes.

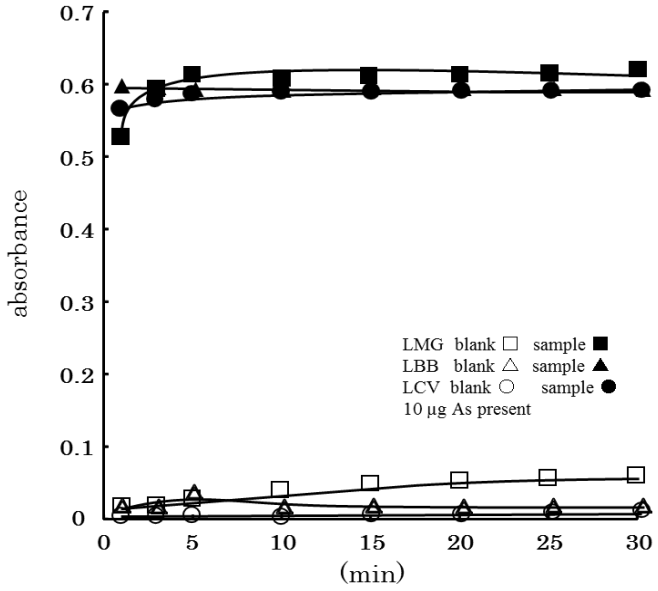

Figure 2: Effect of reaction time of iodine and leuco dyes

3.3. Effect of temperature

The leuco dyes may be easily oxidized with oxygen in solution Therefore, effect of temperature was investigated. The temperature was changed from 10℃ to 40 ℃. As can be seen from Fig.3, the temperature is increased, the absorbance was also increased. In these leuco dyes, the increment ratio of absorbance for LMG, LCV and LBB, at 10 ℃ to 30 ℃ were obtained 27.6%, 23.2% and 10.9% respectively. The temperature effect is most small in the case of LBB. Moreover, the increment of absorbance of blank value was lowest for LBB. From these result, less susceptible reagent for temperature was LBB.

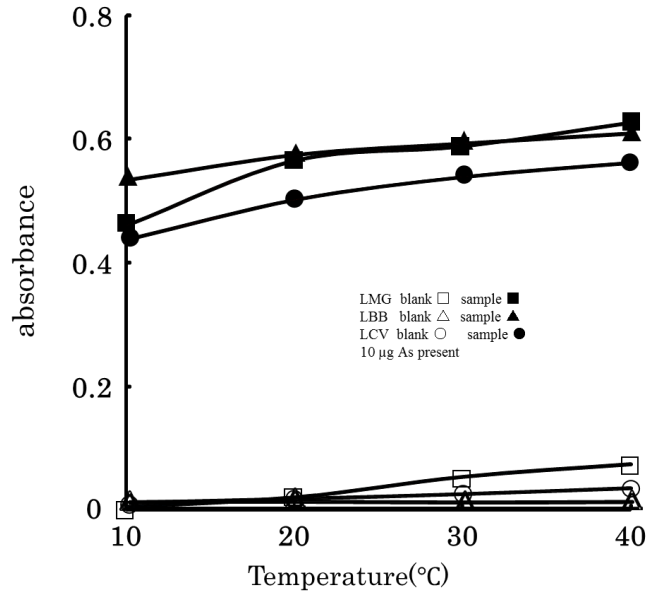

Figure 3: Effect of temperature

3.4. Effect of amounts of iodate

As shown in reaction, iodate oxidize the As (III) and iodine was liberated in the strong acid medium. However, it is supposed that the iodate used for the reaction of oxidation with arsenic (III) was present in the reaction of iodine and leuco dyes. Therefore, the effect of amounts of iodate amounts was investigated (Fig.4); as seen from Fig.4, the effect of iodate on the absorbance was most small when used LBB as reagent.

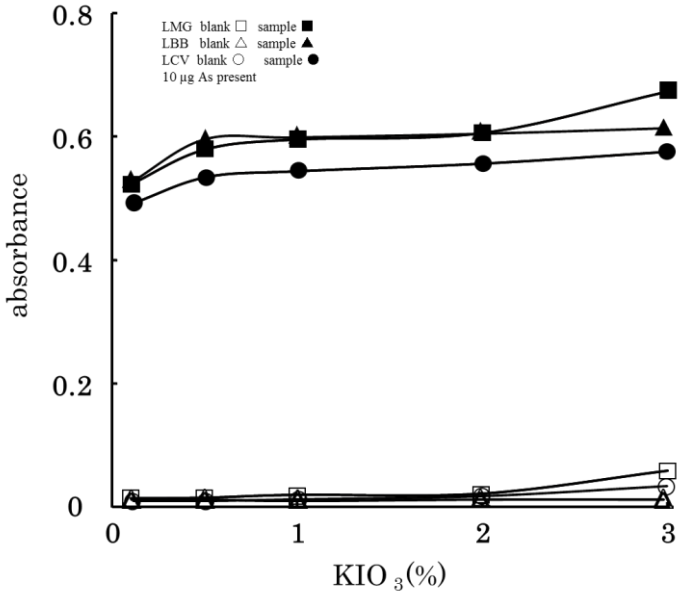

Figure 4: Effect of iodate concentration

3.5. Effect of amounts of leuco dyes

Leuco dyes were oxidized with iodine and color developing have obtained. In these reaction, the effect of amount of leuco dyes was investigated (Fig.5); as seen in Fig.5, the absorbance of blank and sample indicated as red color of LMG were increased sharply more than 0.04%. However, other two reagents for LCV and LBB were indicated same.

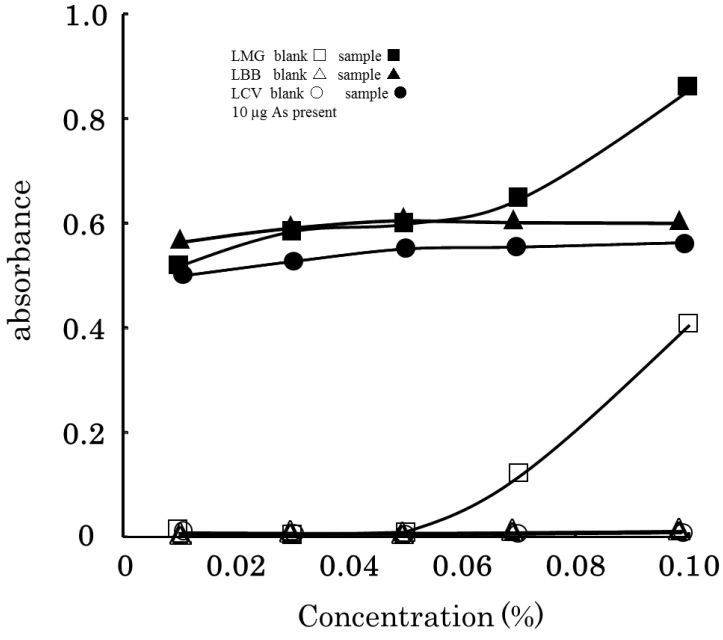

Figure 5: Effect of leuco dye concentration

3.6. Calibration curves

Linear calibration curves were obtained using a standard procedure. Beer's law is obeyed in the range of 0.1-0.1μg mL^{-1} as arsenic. Molar absorbance (molar extinction coefficient) for LMG, LCV and LBB were 4.42×10^4 l mol^{-1} cm^{-1}, 4.11×10^4 l mol^{-1} cm^{-1} and 4.46×10^4 l mol^{-1} cm^{-1} respectively.

3.7. Effect of foreign ions

Validity of the method was assessed by investigating of the effect of various foreign ions. The 2μg of arsenic (III) was taken and the foreign ions in amount of 10 folds and 100 folds were examined. The result shown in Table 1; as seen in Table 1, iron (Ⅲ) was influenced on the determination of As (Ⅲ) determination. However, other ions contains commonly presented in environmental sample solution were not influenced to the method.

Table 1: Effect of foreign ions on determination of 2μg of As (Ⅲ)

Foreign ion	LMG		LCV		LBB	
	Interference (%)		Interference (%)		Interference (%)	
	2μg mL^{-1}	20μg mL^{-1}	2μg mL^{-1}	20μg mL^{-1}	2μg mL^{-1}	20μg mL^{-1}
Na^+	-3.6	-1.8	0	-1.8	1.7	-2.6
K^+	-1.5	-3.7	0	3.6	-1.7	-3.5
Mg^{2+}	5.3	1.5	-2.6	-4.4	-0.9	-0.9
Ca^{2+}	-2.1	7.1	-2.6	-0.9	-0.9	0.9
Mn^{2+}	1.5	8.4	4.4	6.1	0	1.8
Fe^{3+}	-6.3	-24	-4.3	-11.2	27.7	542.9
Cl^-	4.7	0.8	0	-0.9	1.7	0
NO_3^-	0.8	0	0.9	-0.9	0	0
HCO_3^-	-3.8	-1.5	-1.7	-1.7	-3.4	-4.3
SO_4^{2-}	-4.7	-3.9	-1.8	0	3.4	3.4
PO_4^{3-}	-6.5	-6.5	-3.5	-4.4	-0.9	0

4. CONCLUSION

A comparative study of leuco dyes for use as color developing reagents for the determination of As(Ⅲ) was carried out. The effects of analytical parameters, such as pH and temperature were examined. Of the leuco dyes studied, LBB was considered the most suitable dye for the determination of As(III) since the absorbance was not influenced by variation in pH and temperature; it also demonstrated high sensitivity, obeying Beer's law in the range 0.1-0.1μg mL^{-1} for As. The molar extinction coefficient of LBB dye was determined to be 4.46×10^4 l mol^{-1} cm^{-1}.

ACKNOWLEDGEMENT

This work was supported by Kogakuin university grant.

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