

# CHAPTER I

## INTRODUCTION



### 1.1 Problem Definition

Visible spectrometry is based on measuring the absorption of visible radiation by molecules (1). Visible light represents a very small part of electromagnetic spectrum and is generally considered to extend from 380 to 780 nm. The visible spectrometric technique is widely used for the determination of metals, cationic species, anionic species and complex ions. Although atomic spectrometric techniques are most commonly used to determine metals because of their better selectivity and detectability. However molecular spectrometric instrumentation (spectrometer) is now fairly cheap, and certainly much cheaper than most other spectrometric instruments used in analysis. Spectrometric techniques can be used to determine metal ions with specific oxidation states. Viewing in term of the popularity of the method, the spectrometric determinations of metal can be performed based on the selective formation of a metal complex between a metal cation and an organic ligand, and a redox reaction between a metal cation and an organic reagent.

Metal cations, which absorb weakly or not at all in the visible region, can be changed into strongly colored compounds by means of metallochromic reagents or colored complexing agent. Numbers of these substances have been proposed as indicators for complexometric titration and as metallochroms for spectrometric determination of metal-ion.

Metallochromic reagents, which give the color reactions upon which spectrometric methods are based, are called spectrometric reagents (2), which can be grouped into two categories: organic and inorganic. These reagents can be classified into many groups, namely dithizone, azo, triphenylmethane and xanthene, dithiocarbamates, 8-hydroxyquinoline and derivatives, formaldoxime, and thiocyanate. Most spectrometric reagents in visible spectrometry are based on

organic reagent. Among these, azo dyes are widely used because they give intense color and the metal-azo complexes have high molar absorptivity ( $\epsilon > 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) hence giving high sensitivity of the spectrometric method.

Azo dyes may broadly be divided into monoazo, disazo, trisazo, tetrakisazo and polyazo compounds.

Azo derivatives with chromotropic acid as central molecule (including monoazo, disazo and bisazo) (3) are at present widely used for the spectrometric determination of more than 30 elements. These reagents are noted for their high sensitivity (high molar absorptivity) and the color after chelation generally gives greater bathochromic shift of approximately 50-150 nm. With some of these reagents, the selective visible spectrometric determinations through complexation of readily hydrolysed elements (Zr, Th, Nb, Bi, *etc.*) in acidic media, are possible.

However it reveals that less studies have been carried out on bis-O,O'-dihydroxyazo derivatives of chromotropic acid with nitro-group as auxochromes presented in aromatic rings of diazo compounds. For example, Varothai (4) showed that 2,7-bis[(2-hydroxy-3-nitro-5-sulfohenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid gave the color reaction to bismuth(III) with reasonably high sensitivity without the interference of lead(II). Mean while, the literature reviews from 1991-1997 showed that, in visible spectrometric determination of bismuth(III), as shown in Table 1.1 and Figure 1.1, no nitro derivatives of bis-O,O'-dihydroxyazo of chromotropic acid have been used as metallochromic reagents. Therefore it is reasonable that this study should be carried out aiming at the synthesis and the study of the metallochromic properties of these nitro derivatives of bis-O,O'-dihydroxyazo of chromotropic acid.

**Table 1.1** Metallochromic reagents for bismuth(III) from 1991-1997

Reagents	Stioch. M : L	Condition	$\lambda_{\max}$ (nm)	$\epsilon$ L cm <sup>-1</sup> mol <sup>-1</sup>	Adherence to Beer's law	Ref.
<b>1991</b>						
1) Tribromochlorophosphonazo	1:2	pH 2.4	640	$1.05 \times 10^5$	0-10 $\mu\text{g Bi}/25 \text{ mL}$	5
2) Chlorophosphonazo-PN	-	In strong HClO <sub>4</sub>	713	$9.84 \times 10^4$	-	6
3) <i>p</i> -Methyldibromoarsenazo	-	In HClO <sub>4</sub>	630	$8.75 \times 10^4$	0-1 $\mu\text{g Bi}/ \text{ mL}$	7
4) Tribromoarsenazo	1:2	In 0.56M HNO <sub>3</sub>	635	$8.42 \times 10^4$	0-0.80 $\mu\text{g Bi}/ \text{ mL}$	8
<b>1992</b>						
5) Arsenazo-DBS	-	-	630	-	0-15 $\mu\text{g Bi}/25\text{mL}$	9
6) Dibromo- <i>p</i> -nitrochlorophosphonazo	1:2	In 0.02-1.5 M HClO <sub>4</sub>	620	$6.44 \times 10^4$	0-60 $\mu\text{g Bi}/25\text{mL}$	10
7) Chlorophosphonazo- <i>mN</i>	-	-	666	$7.73 \times 10^4$	-	11
<b>1993</b>						
8) 2,6-Dibromoarsenazo	-	In HClO <sub>4</sub> -H <sub>3</sub> PO <sub>4</sub>	622	$9.9 \times 10^4$	0-16 $\mu\text{g Bi}/25\text{mL}$	12
9) 5-Bromophosphonazo-TB	-	In HClO <sub>4</sub>	635	$9.4 \times 10^4$	0-25 $\mu\text{g Bi}/25\text{mL}$	13
<b>1994</b>						
10) Dibromocarboxyarsenazo	-	In 0.04-0.16 M HClO <sub>4</sub>	625	$7.2 \times 10^4$	0-0.5 $\mu\text{g Bi}/\text{mL}$	14
11) 4BPA-TB	-	In HClO <sub>4</sub>	644	$1 \times 10^5$	0-20 $\mu\text{g Bi}/25\text{mL}$	15
<b>1995</b>						
12) Arsenazo III	-	-	615	$5.9 \times 10^4$	0-20 $\mu\text{g Bi}/25\text{mL}$	16
13) Chlorophosphonazo- <i>mI</i>	1:2	In 0.3M HNO <sub>3</sub> -0.15M H <sub>3</sub> PO <sub>4</sub>	680	$1.48 \times 10^5$	0-18 $\mu\text{g Bi}/25\text{mL}$	17
14) Dibromocarboxyarsenazo	-	In 1.2 M HClO <sub>4</sub> -1.5M H <sub>3</sub> PO <sub>4</sub>	635	$8.61 \times 10^4$	0-20 $\mu\text{g Bi}/25\text{mL}$	18

**Table 1.1 (cont.)**

Reagents	Stioch. M : L	Condition	$\lambda_{\max}$ (nm)	$\epsilon$ L cm <sup>-1</sup> mol <sup>-1</sup>	Adherence to Beer's law	Ref.
<b>1996</b> 15) 2,6-Dibromo-4-ethoxyarsenazo	-	In 1.5M HClO <sub>4</sub>	639	9.67 × 10 <sup>4</sup>	0-25 µg Bi/25mL	19
<b>1997</b> 16) Dibromomethylcarboxyarsenazo 17) <i>p</i> -Acetylchlorophosphonazo	- -	In 0.8M HClO <sub>4</sub> -0.5M H <sub>3</sub> PO <sub>4</sub> In HClO <sub>4</sub>	630 -	1.02 × 10 <sup>5</sup> 5.2 × 10 <sup>4</sup>	0-20 µg Bi/25mL 0-40 µg Bi/25mL	20 21

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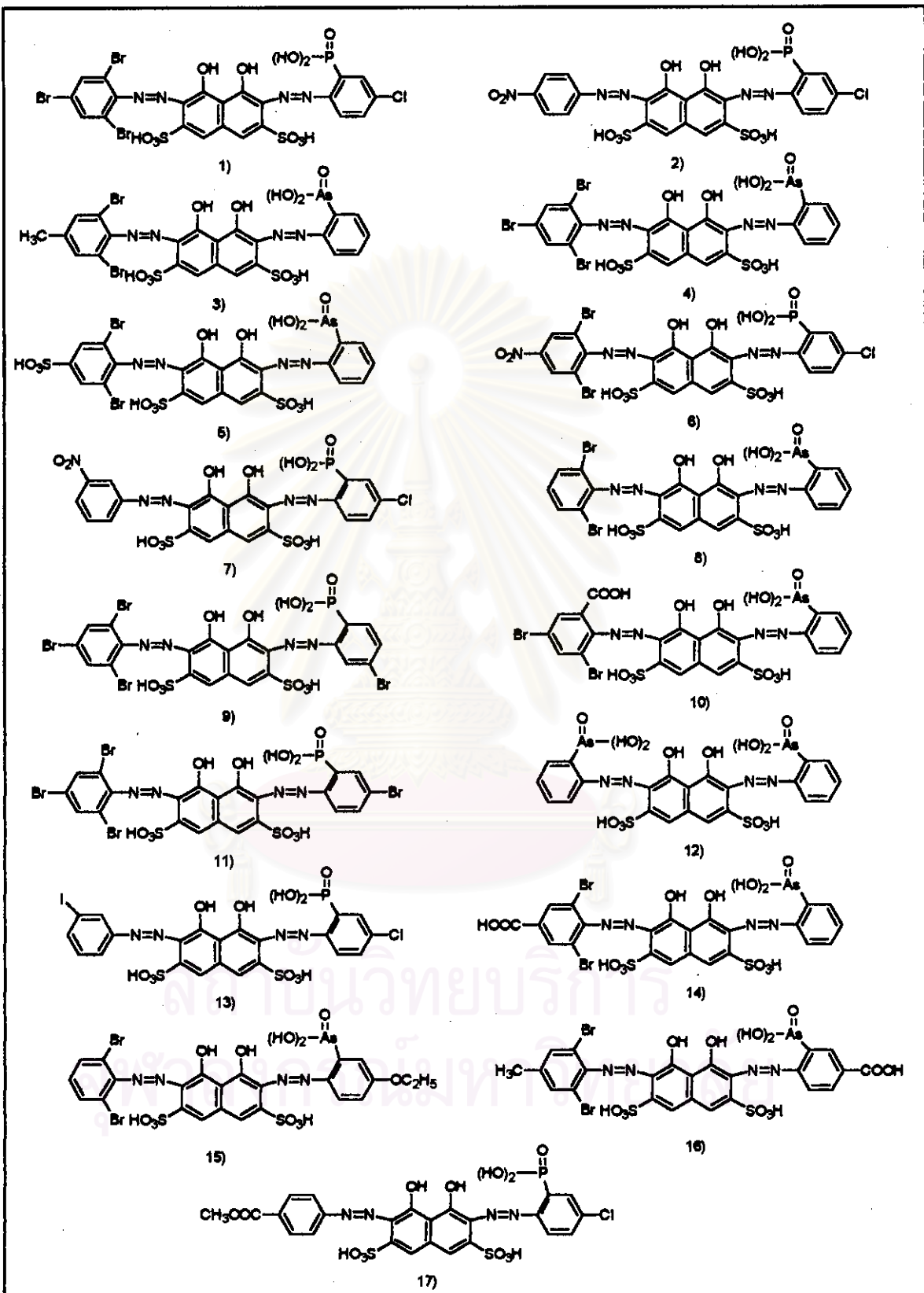


Figure 1.1 Structures of disazo compound

## 1.2 Scope and Objectives

1. To synthesize of the following compounds:
  - 2,7-Bis[(2-hydroxy-5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid
  - 2,7-Bis[(2-hydroxy-4-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid
  - 2,7-Bis[(2-hydroxy-6-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid
  - 2,7-Bis[(2-hydroxy-3,5-nitrophenyl)azo]-1,8-dihydroxy-3,6-naphthalenedisulfonic acid
2. To investigate the metallochromic property of these compounds particularly with bismuth(III).
3. To develop a recommended visible spectrometric method for bismuth(III).

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