RECENT ADVANCES OF THE ASYMMETRIC BISAZO DERIVATIVES OF ARSENAZO AND PHOSPHONAZO AS CHROMOGENIC REAGENTS IN ANALYTICAL CHEMISTRY

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SUMMARY

The asymmetric bisazo derivatives of Arsenazo and Phosphonazo have been widely used as chromogenic reagents in spectrophotometric determination of thorium, uranium, rare earth elements and other heavy metals. They exhibit advantages over the symmetric reagents such as Arsenazo III and Chlorophosphonazo III both in sensitivity and selectivity. The following is a brief introduction and short review on these reagents concerning their structures, analytical characteristics, synthesis, purification and application. 182 references mainly published in the past decade are presented.

INTRODUCTION

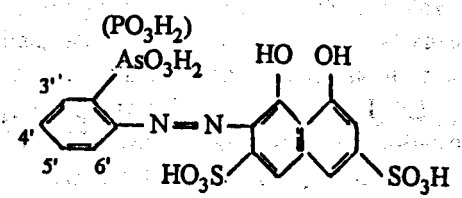
Arsenazo and phosphonazo are azo reagents of chromotropic acid containing the functional groups $-AsO_3H_2$ and $-PO_3H_2$ respectively. Among these reagents, Arsenazo III[1] and Chlorophosphonazo III[2] are the most important. They have been widely used in spectrophotometric determination of uranium, thorium, zirconium and rare earth elements etc. In the past decade, a series of asymmetric Arsenazo and Phosphonazo reagents were synthesized by Chinese analysts. As for rare earth elements, these reagents showed their better selectivity, higher sensitivity and broader range of acidity, as compared with Arsenazo III and Chlorophosphonazo III. Their outstanding properties aroused the interests of analysts.

In this paper, the analytical characteristics concerning the structure, synthesis and purification, as well as their application of these reagents are briefly introduced and reviewed.

STRUCTURES AND THEIR ANALYTICAL CHARACTERISTICS

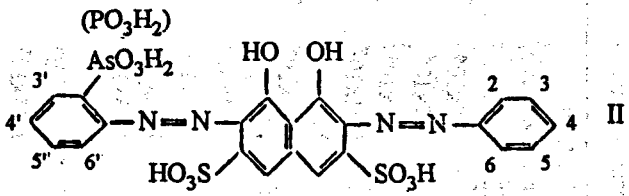
These series of reagents have the general structural formulae as follows:

Monoazo



I

Bisazo



II

The reagents with formula II have the same chromotropic acid-bisazo kernel, but the substituents on the two benzene rings differ. As for Arsenazo III, there are $-AsO_3H_2$ groups on 2'- and 2-positions, while Chlorophosphonazo III has $-PO_3H_2$ groups on 2'- and 2-positions and -Cl groups on 4'- and 4-positions. Both of them have symmetric structures.

Recently, a number of asymmetric bisazo derivatives of Arsenazo and Chlorophosphonazo were synthesized and studied. It was found that the different substituents on different positions of benzene rings will alter the analytical characteristics of reagents. The asymmetric reagents provide advantages (as for rare earths) in the following respects:

(1) *Sensitivity*

When halogen-, nitro-, carboxy- or acetyl- etc. groups are introduced into reagent molecules of bisazo derivatives of Arsenazo or Chlorophosphonazo, especially more than one substituent on the benzene ring which contains no $-AsO_3H_2$ or $-PO_3H_2$, -Cl groups, their sensitivities will be increased remarkably. In the reactions of Cerium(III) with the asymmetric bisazo derivatives of these reagents, the sensitivities are 1-3 times as high as compared with those of Arsenazo III and Chlorophosphonazo III (Table 1).

Table 1.
Comparison of the sensitivities of the reactions of cerium with bisazo reagents of Arsenazo and Chlorophosphonazo

Reagent		Molar Absorptivity	Ref.
Chlorophosphonazo III	CPA III	5.9×10^4	3
p-Nitro-chlorophosphonazo	PNCPA	8.7×10^4	3
m-Nitro-chlorophosphonazo	MNCPA	9.3×10^4	4
m-Acetyl-chlorophosphonazo	MACPA	1.01×10^5	3
m-Carboxy-chlorophosphonazo	MKCPA	1.05×10^5	3
Trichloro-chlorophosphonazo	TCCPA	1.08×10^5	5
Dibromo-nitro-chlorophosphonazo	DBNCPA	1.09×10^5	6
Arsenazo III	AA III	4.7×10^4	7
p-Acetylarsenazo	PAAA	1.16×10^5	8
Trichloroarsenazo	TCAA	1.23×10^5	9
Dibromo-sulfo-arsenazo	DBSAA	1.22×10^5	10
Dibromo-chloro-arsenazo	DBCAA	1.29×10^5	11
Tribromoarsenazo	TBAA	1.33×10^5	12
Dibromo-carboxy-arsenazo	DBKAA	1.40×10^5	13

(2) *Absorption spectrum*

In general, the asymmetric bisazo derivatives resemble the symmetric reagents, their rare earth complex gives two absorption maxima, one is higher than the other. Reagents containing different substituents yield different shapes in their absorption spectra. For instance, *p*-Nitro-chlorophosphonazo, PNCPA (the abbreviation of 3-[(4-chloro-2-phosphono-phenyl)azo]-6-[(4-nitro)azo]-4,5-dihydroxy-2,7-naphthalene-disulfonic acid) reacts with yttrium in 0.2-0.5M $HClO_4$ to form a complex which exhibits a special absorption spectrum with a peak at 730nm (Fig. 1). It is distinguished from other rare

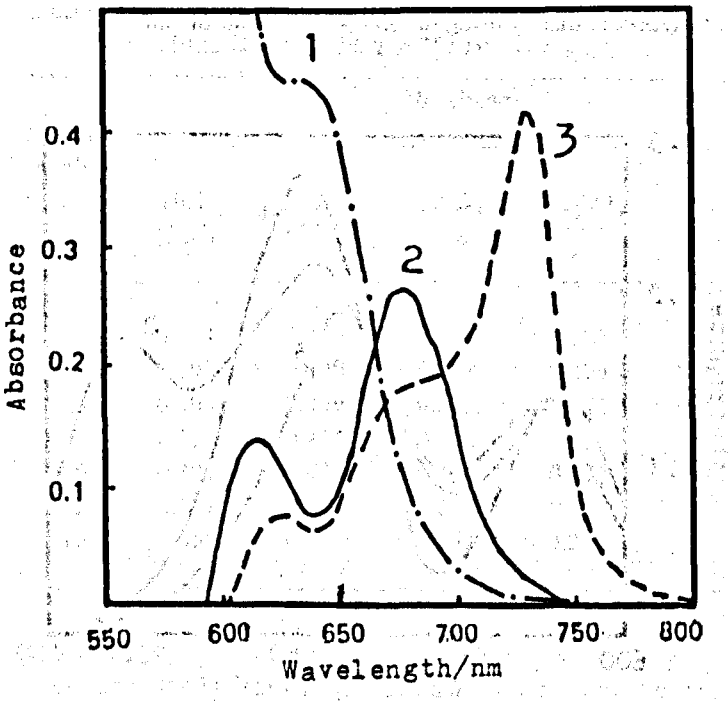


Fig. 1 Absorption spectra of PNCPA complexes of Ce and Y.
1, PNCPA against water; 2, Ce-PNCPA against reagent blank; 3, Y-PNCPA against reagent blank.
Ce, 10.0μg; Y, 10.0μg; 2M $HClO_4$, 1.0ml; 0.03% PNCPA, 2.0ml.

earths (from La to Lu) and can be used for the determination of yttrium in rare earth mixture[14]. P-Acetyl-chlorophosphonazo, PACPA forms with all the rare earth elements complexes with an isosbestic point at 667nm (Fig. 2). At this wavelength, the values of absorbencies of complexes with equal amounts of rare earths are almost identical, and the method using PACPA has been used to determine total rare earths in samples of different compositions[15].

The reagent having more than one substituent on the benzene ring which contains no $-AsO_3H_2$ or $-PO_3H_2$, -Cl groups forms a complex with the rare earth and gives only one peak in its absorption spectrum. The peak of the complex is usually shifted to the shorter wavelength with respect to that by using reagent with one substituent.

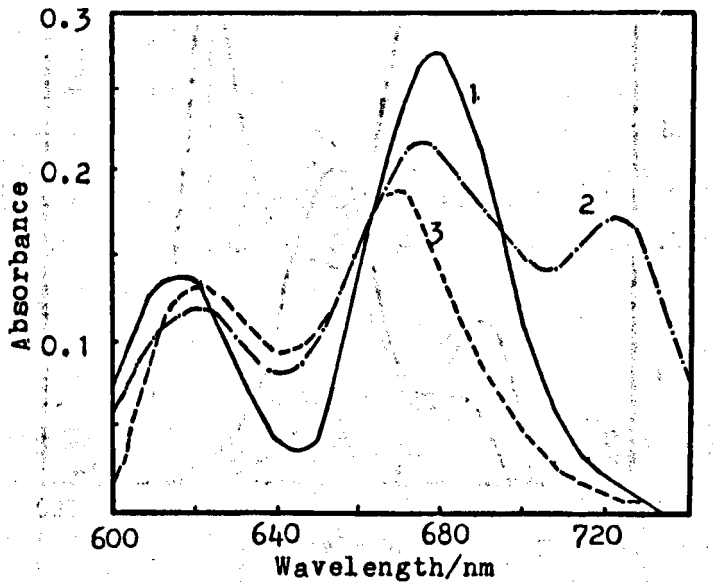


Fig. 2 Absorption spectra of PACPA complexes of rare earths:
1, Ce-PACPA; 2, Y-PACPA; 3, YB-PACPA against reagent blank. Ce, Y and Yb, 10μg each;
PACPA, 5.29×10^{-5}M; HCl, 0.2M.

(3) *Acidity of reaction*

The asymmetric reagents react with rare earths in high acidic medium. For example, Dibromocarboxyarsenazo, DBKAA (the abbreviation of 3-[(2-arsonophenyl)azo]-6-[(4,6-dibromo-2-carboxyphenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulfonic acid) gives a sensitive color reaction with the cerium subgroup rare earths in media of various acids (hydrochloric, perchloric, nitric, sulphuric and phosphoric acid) with wide ranges (Table 2). It is very convenient for sample treatment and control of acidity in color development.

Table 2.

Effect of amounts of various acids on the cerium-DBKAA reaction[13] (10μg Ce were added in 25ml of solution)

Acid added (ml)	Absorbance				
	HCl (6 M)	$HClO_4$ (6 M)	HNO_3 (6 M)	H_2SO_4 (3 M)	H_3PO_4 (2 M)
1	0.404	0.409	0.410	0.388	0.402
3	0.397	0.409	0.389	0.399	0.391
5	0.400	0.409	0.375	0.391	0.390
7	0.397	0.404	0.352	0.389	0.389
9	0.377	0.409	0.323	0.372	0.386
12	0.371	0.409	0.256	0.372	0.385
15	0.359	0.401	0.161	0.362	0.392

(4) *Selectivity*

Owing to the high acidity which is allowed for the reactions of the asymmetric reagents with rare earths, the selectivity of the reaction will be improved noticeably. Usually, the tolerance limits of common ions increase to several milligrams or even to several tens of milligrams (Table 3). Thus, the rare earths in many samples can often be determined directly without separation.

Table 3.

Comparison of the selectivities of the reactions of cerium with certain bisazo derivatives of chromotropic acid[12]

Reagent	Tolerance amount of foreign ion (mg)									
	Ca^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}	Cu^{2+}	Mn^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Cr^{3+}
AA III	0.21	24.8	0.005	0.1	0.1	40.0	1.0	60.0		0.05
CPA III				1.0	0.2	1.0	1.0		0.1	1.0
MACPA	0.02	0.5		0.05	0.1	0.5	0.5	0.5		0.1
TCCPA	0.09	20.0	3.5	1.8	4.0	20.0	15.0	20.0	20.0	5.0
DBCCPA*			18.0	20.0		70.0	25.0		35.0	8.0
TCAA	10.0	8.0		60.0	12.0	120	8.0	30.0	40.0	15.0
TBAA	0.6	40.0	3.0	26.0	5.6	15.5	6.0	30.0	10.0	1.5
DBCAA	5.0	50.0	43.0	4.5	18.0	70.0	50.0		20.0	8.5
DCBAA**	5.0	10.0		1.0		50.0	2.0		40.0	5.0
DBSAA	0.2	50.0	30.0	100	4.0	10.0	30.0	10.0	10.0	3.0

* Dibromo- chloro-chlorophosphonazo

** Dichloro-bromo-arsenazo

As certain substituents are introduced into these reagents, it is found that not only their sensitivities increase, but the selectivities are raised as well. Arsenazo III is a well-known reagent for thorium, but the tolerated amount of uranium(VI) is low. However, the asymmetric bisazo reagents such as Tribromoarsenazo (TBAA) and Dibromo-o(p)-nitro-arsenazo (DBONAA, DBPNAA) are more selective in respect to uranium in the determination of thorium (Table 4).

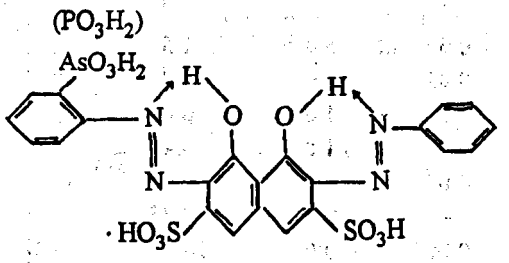
Table 4.
Comparison of the selectivities of bisazo reagents for thorium

Reagent	Tolerance amount of foreign ion (mg)				Ref.
	La	Y	U(VI)	Ca	
DBONAA	0.5	5.0	1.5	50	16
DBPNAA	0.03	5.0	3.0	50	17
AA III	0.5	1.0	0.06	10	7
PAAA	0.07	1.8	0.4	14	18
MSCPA*	0.07	0.3	0.1	5	19
MNNPA**	---	0.23	0.25	---	20
TBAA	0.003	0.01	10.0	0.5	21
PBCPA***	****	****	0.1	6.0	22
CPA III	---	0.02	0.001	10.0	23

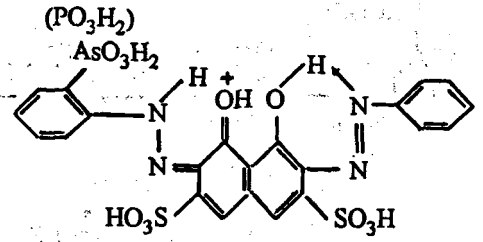
* *m*-Sulfo-chlorophosphonazo
** *m*-Nitro-nitrophosphonazo
*** *p*-Bromo-chlorophosphonazo
**** interfere seriously

The absorption spectra of the asymmetric derivatives of Arsenazo and Phosphonazo will vary in different acidic solutions. For instance, *m*-Nitrochlorophosphonazo (MNCPA) is rosy-red in a less than 0.5M solution of hydrochloric acid with a maximum absorption at 545nm, and will turn to purplish-blue in pH 11.3 solution with an absorption peak at 590nm due to the dissociation of one proton from -OH on the naphthalene ring of the reagent. In 7.5M sulphuric acid solution, the reagent is protonated as a green species and its absorption peak will shift to 660nm.

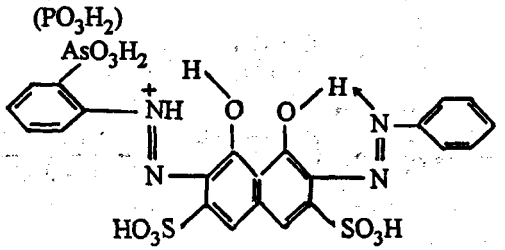
The variation of the spectra in solutions of various acidities indicates that the structure of reagent changes in different media. According to the calculation by quantum chemistry [19, 24-25], it may be assumed that the principal species of these asymmetric reagents in weakly acidic solution exists as



and the two following species may exist in strongly acidic medium:



(I)

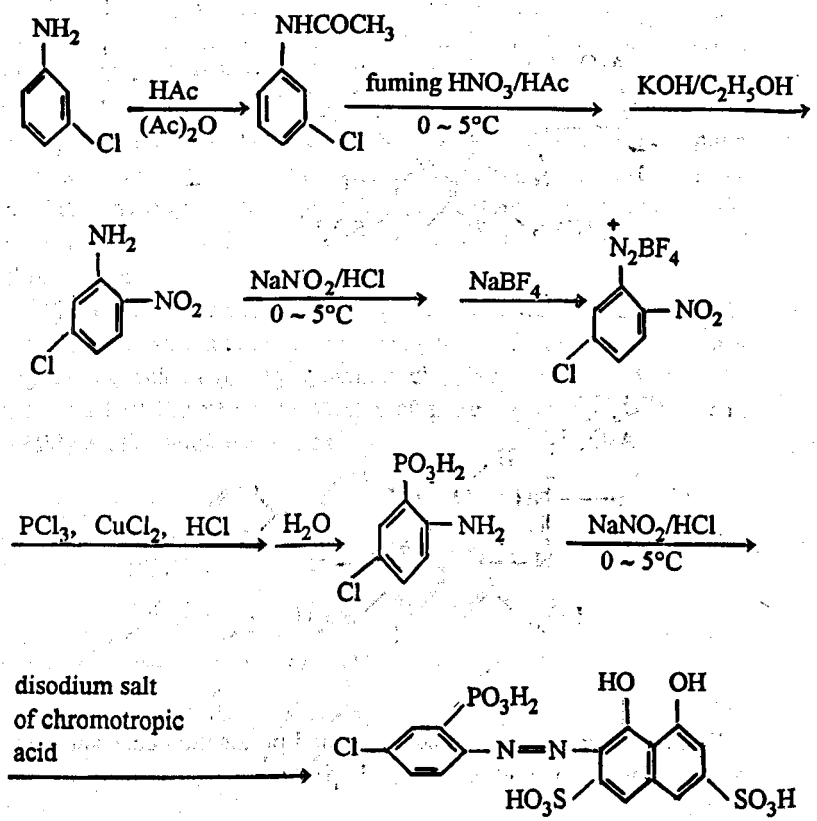


(II)

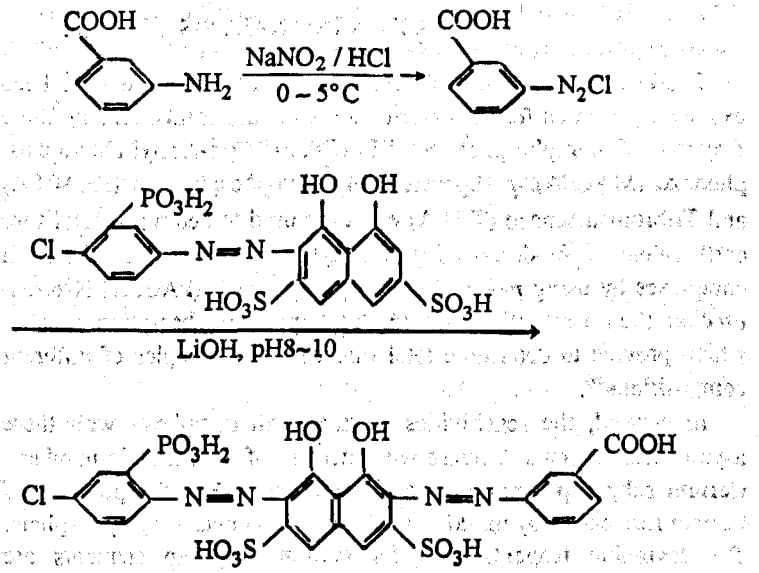
The stepwise dissociation constants and protonation constants can be determined by potentiometric and spectrophotometric methods [26-32]

SYNTHESIS AND PURIFICATION

The methods for synthesis of various reagents is different according to their structures. In general, the corresponding arylamine is synthesized at first. After the diazotization of arylamine and coupling with chromotropic acid, monoazo derivative will be obtained. The synthetic reaction of Chlorophosphonazo I is outlined as follows:



If the arylamine with different substituents is diazotized and coupled with monoazo derivative in the presence of catalysts such as LiOH, Li_2CO_3 or $Ca(OH)_2$ etc., a series of asymmetric bisazo derivative with different substituents can be synthesized. The outline for synthesis of m-Carboxychlorophosphonazo (MKCPA) is shown as follows:



It should be noticed that the multi-substituted arylamine will be diazotized in strong acid medium (e.g. sulphuric acid). The syntheses of reagents with multi-substituents may be found in references 12, 13, 16, 33.

When monoazo derivatives are prepared with *m*-fluoroaniline or aniline with halogen or nitro groups in *para* position, some new series of reagents will be synthesized. The works on these derivatives as reagents for rare earths has been proceeding in recent years[34-39].

High-purity reagents are always required for the determination of their constants and research work on the mechanism of the reactions. Thin-layer chromatography, extraction and recrystallization are the methods often used for purification of these reagents. Extraction seems to be more effective and simple; it usually gives a higher yield and has been widely used [4, 40-42]. The purity of reagents is often controlled and checked by paper chromatography, IR spectroscopy, element analysis and their sensitivities of the colour reactions, etc.[40, 43-45].

APPLICATION IN ANALYSIS

The bisazo derivatives of Arsenazo and Phosphonazo have been extensively studied for the determination of rare earths. Among these reagents, Chlorophosphonazo III (CPAIII), *m*-Acetyl-chlorophosphonazo (MACPA), *p*-Hippuric acid chlorophosphonazo (PHACPA) and Tribromoarsenazo (TBAA) etc. were used to determine total rare earth elements. As described previously, the absorbency of rare earth complexes by using *p*-Acetyl-chloro-phosphonazo (PACPA) is measured at their isosbestic point (667nm) on their absorption spectra, which provide to determine total rare earths in samples of different compositions[46].

In general, the sensitivities of rare earth complexes with these asymmetric reagents decrease with increase of their atomic numbers. Cerium subgroup rare earths can be determined in the presence of heavier rare earths by masking with oxalic acid and/or pyrophosphate. The favorable reagents used for cerium subgroup elements are Dibromo-nitro-chlorophosphonazo (DBNCPA), *m*-Carboxy-chlorophosphonazo (MKCPA), *m*-Nitro-chloro-phosphonazo (MNCPA) and Dibromo-carboxy-chlorophosphonazo (DBKCPA) etc.

The derivatives of Arsenazo and Phosphonazo react with rare earths in weak acid medium to form special β-type complexes, those often give better selectivities and higher sensitivities. Study on the β-complex formation reactions of rare earths with these reagents is a new research area. For instance, the β-complex formed between yttrium and *p*-Nitro-chlorophosphonazo (PNCPA) allows to determine yttrium in the presence of certain amounts of lanthanides, and has been widely used [47-51]. The β-complex reaction of *p*-chloro-chlorophosphonazo (PCCPA) with scandium and heavier rare earths is very sensitive and gives satisfactory results in the determination of these elements [42, 52].

Some derivatives of Arsenazo and Phosphonazo can form ternary complexes with rare earths in the presence of surfactants, and thereby the selectivities and sensitivities further increase [53-56]. Moreover, studies on the multi-nuclear complexes formed by these reagents with rare earths and other metal such as Mo(VI), Cu(II) etc. have been also reported [57-59].

Determination of rare earths with asymmetric bisazo derivatives of Arsenazo and Phosphonazo by ion-exchanger phase spectrophotometry is selective and sensitive, due to selective sorption and concentration of rare earths in the resin phase [60-61].

These reagents have also been used for the determination of zirconium, titanium, bismuth, beryllium, calcium, magnesium and aluminum, etc.

The analytical characteristics and applications of these reagents are listed in Tables 5 and 6.

Table 5.
Spectrophotometric characteristics of phosphonazo reagents

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	Ex10^{-4}	Ref.
Chlorophosphonazo III (CPA III)	-Cl(4,4') -PO_3H_2(2)	Zr	CTMAB, HCl, 1.4M	685	4.3	62
		V	pH 4.3	610	1.8	63
		Ca	C_2H_5OH	663	6.8	64
		ΣREE	pH 1	677	5.5-8.4	65-67
			CTMAB, pH 4.8	703		68
		Y	HNO_3, 0.2M	670	12.0	69
		Gd	pH 1	640		70
		Sc	OPB, HCl, 0.15M	700	2.25	71
		Cr(III)	pH 4.5-5.7	620	2.1	72
		Pd(II)	H_2SO_4, 1.2M	625	2.6	73

m-Nitro chlorophosphonazo (MNCPA)	-Cl(4') -NO_2(3)	Ca	pH 6.0-7.8	600	2.44	74
		ΣREE	pH 1.8	670	7.8-8.2	75-77
		ΣCe	pH 1.6	666	9.3-9.5	4
		Sc	TPC, HNO_3, 0.2-0.5M HNO_3	677	4.5	78
			0.3-0.9M	727	10.6	79
p-Nitro-chlorophosphonazo (PNCPA)	-Cl(4') -NO_2(4)	Y	HCl, 0.1M	730	8.49	14,80,81
		ΣY	$HClO_4$,0.08M	735	6.2-9.3	82-83
		ΣCe	pH 1	675	7.1	83-85
		Th	CPC, pH 1	705	16.2	86
m-Acetyl-chlorophosphonazo (MACPA)	-Cl(4') -$COCH_3$(3)	ΣREE	pH 1.0	662	8.0-10.0	87-88
		ΣCe	CPB, pH 1.0	670		89
		Ca	pH 6.6-6.8	606		90
		U(VI)	pH 3.5	660	3.7	91
		Sc	HCl, 0.3M	718	3.1	92-93
		Ti	HCl, 0.08M	673	3.92	94

Table 5., continued (2)

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	$Ex10^{-4}$	Ref.
p-Acetyl-chlorophosphonazo (PACPA)	-Cl(4') $-COCH_3$	ΣREE	HCl, 0.2M	667		15,95
m-Carboxy-chlorophosphonazo (MKCPA)	-Cl(4') -COOH(3)	ΣCe	HCl, 0.1M	670	10.5	3,96-97
		Sc	HCl, 0.2M	665	4.0	92,98
		Th	H_2SO_4, 0.1M	676	10.3	99
			CPC, HCl, 0.04-0.72M	685	15.0	100-101

p-Bromo-chlorophosphonazo (PBCPA)	-Cl(4') -Br(4)	Th Be Ca(Mg)	HNO_3-$H_2C_2O_4$ PVA, pH 9.3 pH 10.2-10.5	680 615 575	8.6 3.15 1.2	102 103 104
p-Chloro-chlorophosphonazo (PCCPA)	-Cl(4,4')	Y ΣY ΣREE Sc Bi	pH 4.5 pH 4.7 HCl, 0.16M pH 2.1 HNO_3, 0.24M	746 746 665 762 675	15.6 12.5-16.4 15.4 8.9	41 105 106 107-108 109
m-Sulfo-chlorophosphonazo (MSCPA)	-Cl(4') -SO_3H(3)	Th Ce	HCl, 1.9M H_2SO_4, 0.5M H_2SO_4, 0.05M	670 670 650	10.1 7.0 3.9	19 110 111

Table 5, continued (3)

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	Ex10^{-4}	Ref.
p-Iodo-chlorophosphonazo (PICPA)	-Cl(4') -I(4)	Bi ΣREE	HCl, 0.2M	690 680	2.2 9.7-10.8	112 113-115
p-Methyl-chlorophosphonazo (PMCPA)	-Cl(4') -CH_3(4)	Y	pH 5	755	18.2	116-117
p-Sulfoamido-chlorophosphonazo	-Cl(4') -SO_2NH_2(4)	ΣREE	HCl, 0.2M CTMAB, HCl, 0.18M	670 680	8.1-10.3 18.6	118 119
		Cr(VI)		535	2.8	120

p-(*m*-) Formyl-chlorophosphonazo (P(M)FCPA)	-Cl(4') -CHO(4) or -CHO(3)	ΣREE Y	HCl, 0.1M pH 3.5	670 700	8.0-10.0 8.3-13.0	121 121
p-Hippuric acid chlorophosphonazo (PHACPA)	-CL(4') $-CONHCH_2COOH$ (4)	ΣREE Sc Zr	HCl, 0.02-0.05M CTMAB,H_2SO_4, 0.05-0.25M pH 2-3 CPB-C_2H_5OH HCl, 0.25-1.5M	680 682 687 680	7.2-10.2 12.1-18.9 7.8 11.0	122-124 125 126 127
p-Khimdu-chlorophosphonazo (PKhCPA)	-CL(4') $-CH_2N(CH_2COOH)_2$ (4)	ΣREE	HNO_3, 0.1M	665	7.2	128
p-Trifluoromethyl-chlorophosphonazo (PTFMCPA)	-Cl(4') $-CF_3$(4)	ΣREE	HCl, 0.08-0.4M	666	10.1-11.3	129-130

Table 5, continued (4)

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	Ex10^{-4}	Ref.
m-Trifluoromethyl-chlorophosphonazo (MTFMCPA)	-Cl(4')	Ce	pH 1	670	8.0	131
	-CF_3(3)	U(VI)	HCl, 0.4M	690	7.9	132
Tribromo-chlorophosphonazo (TBCPA)	-Cl(4)	ΣREE	HCl, 0.08M	650	11.0-12.0	133
	-Br(2,4,6)	Th	OP, HCl, 3.2M	646	11.5	134
		Pd	H_2SO_4, 1.5-4.0M	617		135
		Bi	pH 2.4	640	10.5	136

Trichloro-chlorophosphonazo (TCCPA)	-Cl(4') -Cl(2,4,6)	ΣREE	HCl, 0.4M	641	8.6-11.7	5
Dibromo-nitro-chlorophosphonazo (DBNCPA)	-Cl(4') -Br(2,6) -NO_2(4)	ΣCe	$HClO_4$, HCl or H_2SO_4, 0.4M	642	10.8	137-141
		Zr	HCl, 1.5M	639	3.5	142
Dibromo-sulfo-chlorophosphonazo (DBSCPA)	-Cl(4') -Br(2,6) -SO_3H(4)	ΣREE	HCl, 0.12M	643	6.8-13.5	143
Dibromo-chloro-chlorophosphonazo (DBCCPA)	-Cl(4,4') -Br(2,6)	ΣREE Zr	HCl, 1.3M CTMAB, C_2H_5OH	645	10.0-12.4	144
			HCl, 1.1M	650	6.3	145

Table 5, continued (5)

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	Ex10^{-4}	Ref.
m-Nitro-nitrophosphonazo (MNNPA)	-NO_2(3,4')	Th	HNO_3, 0.3-0.4M	665	11.7	20
m-Bromo-nitrophosphonazo (MBNPA)	-NO_2(4') -Br(3)	Y	NaAc-HCl	710	7.9	146
p-Sulfoamido-bromophosphonazo (PSABPA)	-Br(4') -SO_2NH_2(4)	ΣREE	CTMAB-C_2H_5OH HCl, 0.12M	679 670	18.0 9.1	147 148

m-Carboxy-bromophosphonazo (MKBPA)	-Br(4') -COOH(3)	Th	HNO_3, 0.05-1.28M	680	8.55	149

ΣREE = Total rare earth elements
ΣCe = Cerium-subgroup rare earths
ΣY = Yttrium-subgroup rare earths
CTMAB = Cetyltrimethylammonium bromide
OPB = n-Octylpyridinium bromide
CPB = Cetylpyridinium bromide
CPC = Cetylpyridinium chloride
TPC = Tetradecylpyridinium chloride
PVA = Polyvinyl alcohol
OP = p-Octylpolyethyleneglycol phenylether
* Refer to formula II on page 4

Table 6.
Spectrophotometric characteristics of arsenazo reagents

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	$Ex10^{-4}$	Ref.
Arsenazo III (AA III)	$-AsO_3H_2(2)$	ΣREE	pH 2.8	650	4.5-7.1	150-151
			C_2H_5OH, pH 0.8-1.5	650	8.1-12.6	152
		Ce	pH 3.1-3.5	610		153
		La	pH 3.1-3.5	655		154
		Zr(Hf)	C_2H_5OH, HCl, 4.3 M	665	14.9(15.3)	155
p-Acetyl-arsenazo (PAAA)	$-COCH_3(4)$	ΣCe	pH 2.0-2.5	670	10.3-11.6	156-158
		Sc	TPC, pH 2.5	689	7.65	159

p-Bromo-	-Br(4)	ΣCe	pH 4.7	713	26.0-35.0	160-161
arsenazo		ΣREE	Triton X-100,			
(PBAA)			pH 5.06	710	24.5	162
Dibromo-chloro-	-Br(2,6)	ΣREE	HCl, 1.0-2.0M	630	13.0	163
arsenazo	-Cl(4)	ΣCe	HCl, 1.2M	640	9.6-11.6	164
(DBCAA)		Y	pH 3.0	635	1.13	165
Dibromo-sulfo-	-Br(2,6)	Zr	CPB-OP,			
arsenazo	$-SO_3H$(4)		HCl, 0.24M	617	6.37	166
(DBSAA)		ΣCe	HCl, 0.32M	630	10.6-12.3	10,167-168
		Bi	H_2SO_4, 1.0M	630		169
		Ba	HCl, 0.08		6.48	170
Tribromo-	-Br(2,4,6)	ΣREE	pH 3.2	630	7.6-11.2	171-172
arsenazo		ΣCe	HCl, 0.1-1.0M	630	12.0-13.7	173-174
(TBAA)		Ba	pH 9.6-11.3	604	2.75	175
		Sr	HCl, 0.48M	620	6.86	176

Table 6, continued (2)

Reagent	Substituent and its position*	Element	Medium and acidity	λ (nm)	Ex10^{-4}	Ref.
Dibromo-fluoro-arsenazo (DBFAA)	-Br(2,6) -F(4)	ΣCe	HCl, 1.5M	630	12.8	177
Dibromo-methyl-arsenazo (DBMAA)	-Br(2,6) -CH_3(4)	ΣREE	pH 1.6-2.8	635	10.1-13.8	178
Dibromo-o-nitro-arsenazo (DBONAA)	-Br(4,6) -NO_2(2)	Th	HCl, 0.12-1.0M	640	9.7	16, 179

Dibromo-p-nitro-arsenazo (DBPNAA)	-Br(2,6) $-NO_2$(4)	Th	HCl, 0.5-1.5M	630	10.7	17
Dibromo-carboxy-arsenazo (DBKAA)	-Br(4,6) -COOH(2)	ΣCe Sr	HCl, 0.1-3.0M pH 2-4	632 622	12.2-14.0 3.8	180-181 182

* Refer to formula II on page 4

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