Advances in the electrochemical determination of gallium(III)

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Electrochemical methods of gallium determination are reviewed. Voltammetric methods are the most widely used and a review of conventional supporting electrolytes and organic reagents available for gallium determination by voltammetry is presented. Several works dealing with gallium ion-selective electrodes have been reported, but only one of them was devoted to a coulometric technique of gallium determination. The electrochemical methods present several advantages over other methods and gallium can be determined in a variety of media such as water, food, soil, rocks, ores, and industrial objects.

Electrochemistry / Gallium / Ion-selective electrode / Mercury electrode / Voltammetry

1. Introduction

The interest in the determination of gallium is connected with its wide use in different fields. The main application of gallium is the production of semiconducting compounds. Gallium arsenide is the most widely used compound among gallium-containing semiconductors [1-4]. The increasing use of gallium arsenide has posed the question concerning its toxicity [3]. The available data indicate that it can be toxic in animals and humans [4,5]. The other application of gallium is as a component of medicinal inorganic therapeutic and diagnostic agents [6]. Hence, there is a need for sensitive and reliable methods for the determination of trace concentrations of gallium in industrial and natural objects [3,7].

There exist a variety of methods for the quantitation of gallium. Electroanalytical methods can be an interesting alternative to other methods for the determination of trace elements. The basis of electrochemical techniques is the measurement of electrical quantities, such as current, potential, or charge, and their relationship to chemical parameters [8]. They have many advantages over other detection systems, namely portable and low-cost instrumentation, high sensitivity, wide linear ranges, selectivity towards electroactive species, speciation capability, and tunability to the characterization of electrochemical information for the system under study [8,9]. Electrochemical techniques have, thanks to their universality, found a broad range of applications, including environmental monitoring, industrial quality control, and biomedical analysis [8].

Electrochemical techniques, in particular voltammetric methods, are widely used for the quantitation of gallium. The electrochemical properties of gallium in different electrolytes have been studied in detail in [10]. The present work proposes a review of our current knowledge and recent advances in electroanalytical methods for gallium determination.

2. Voltammetric methods

2.1. Use of conventional supporting electrolytes

Ga(III) is reduced to Ga(0) in different supporting electrolytes (Table 1) [10-20]. In numerous media it is reduced or oxidized irreversibly [15,16,21]. Meanwhile, different works have reported reversible reduction of Ga(III) in the presence of thiocyanate [13,15-17,22-24], which catalyzes reversible electron transfer [16,22]. Reversibility is achieved by heating the solution to 60-80°C, or by using high ionic strength (6 M) [13,15-17,22-24]. The first thiocyanate used as supporting electrolyte for polarographic gallium determination was mentioned in works summarized in [15]. However, these techniques have relatively low sensitivity ($n \cdot 10^{-5}$ M). Other articles [16,18,23-26] have reported the use of anodic stripping voltammetry (ASV) for Ga(III) determination in thiocyanate solution. Pulse modes of

ASV, which include phase-selective anodic stripping voltammetry (PSASV), square-wave anodic stripping voltammetry (SW ASV) and differential pulse anodic stripping voltammetry (DP ASV), reduce the residual charging current, and consequently lower concentrations of Ga(III) (10^{-9}-10^{-7} M) can be detected. The best sensitivity in SCN^- medium was obtained using differential pulse anodic stripping voltammetry [26] (see Table 1).

Catalyzed reduction of Ga(III) was also observed in the presence of 2,2'-bipyridine [27]. In the presence of both SCN^- and 2,2'-bipyridine higher current peaks were observed [13,15-17,27].

Table 1 Conventional supporting electrolytes for voltammetric determination of Ga(III).

Method [a]	Working electrode [b]	Conditions (supporting electrolyte, pH, temperature)	Linear range / Detection limit, M	Reference
DCP	DME	1 M LiCl, pH 3.0-3.5	$2.9 \cdot 10^{-4}$-$1.4 \cdot 10^{-3}$	[15]
LSP	DME	13 M NH_3 + 2 M NH_4Cl	$1 \cdot 10^{-5}$-$1 \cdot 10^{-3}$	[11]
DCP	DME	1.3 N NH_3 + 1.8 $N(NH_4)_2SO_4$	$1.4 \cdot 10^{-4}$-$4.3 \cdot 10^{-3}$	[15]
DCP	DME	NH_3 + $(NH_4)_2C_2O_4$, pH 8.6-10.0	–	[12]
DCP	DME	0.5 M KSCN + 1.9 M NH_4Cl + 1-2 drops of tropeolin 00, 80°C	$4 \cdot 10^{-5}$	[15]
DCP	DME	NH_4SCN, pH 1.7-3.7, 80°C	–	[13]
DCP	DME	0.25 M glycine / 0.1 M KCl, pH 7.5-8.0	$2 \cdot 10^{-5}$-$1 \cdot 10^{-3}$	[15]
ACP	DME	KSCN + HCl (dilute)	0.5-1.2 mmol	[15]
ACP	DME	$HClO_4$ + NH_4SCN	–	[15]
PSASV	MHDME	1.0 M NH_4SCN, pH 2.0, 60°C	$2.9 \cdot 10^{-7}$	[23,24]
DCP	DME	0.001 M salicylic acid, pH 2.8-3.4	$1 \cdot 10^{-5}$-$5 \cdot 10^{-3}$	[15]
DCP	DME	0.1 M sodium salicylate + 0.1 M NaCl	–	[14]
DPP	DME	acetate buffer, pH 3.5	$7 \cdot 10^{-7}$-$2.4 \cdot 10^{-3}$ / $1.4 \cdot 10^{-7}$	[28]
LS ASV	SMDE	0.1 M salicylic acid + 0.1 M NH_4Cl, pH 3.0	$1 \cdot 10^{-5}$%	[29]
LS ASV	SMDE	0.1 M NaSal	$2 \cdot 10^{-8}$	[15]
LS ASV	SMDE	0.1 M sodium salicylate + 0.1 M KCl, pH 4.0-5.0	$5 \cdot 10^{-6}$%	[15]
LS ASV	Pt	1 M ammonium + 1 M ammonium chloride, pH 9.6 + $8 \cdot 10^{-5}$ M Zn(II)	$1.8 \cdot 10^{-5}$-$3 \cdot 10^{-4}$	[19]
DP ASV	HDME	0.02 M $NaClO_4$ + 0.005 M CH_3COOH, pH 3.2	$5.7 \cdot 10^{-11}$	[17]
DP ASV	HDME	0.005 M salicylate + 0.05 M acetic buffer, pH 4.6	$5.7 \cdot 10^{-11}$	[17]
DP ASV	Ag-Hg FE	0.01 M KSCN, pH 3.05	$5 \cdot 10^{-9}$-$8 \cdot 10^{-8}$ / $1.4 \cdot 10^{-9}$	[26]
PSASV	MHDME	0.5 M NaSCN + 4.5 M $NaClO_4$, pH 2.0	$5 \cdot 10^{-7}$ [c]	[16]
SW ASV	MFE on GCE	0.5 M NaSCN + 1 M $NaClO_4$, pH 2.0	$1 \cdot 10^{-7}$-$1 \cdot 10^{-6}$	[18]
SW ASV	SMDE	0.5 M NaSCN + 4.2 M $NaClO_4$, pH 2.0	$3 \cdot 10^{-7}$-$1 \cdot 10^{-6}$, $1 \cdot 10^{-8}$-$1 \cdot 10^{-6}$ (in the presence of Sb(III))	[25]
SW ASV	BiFE	buffer solution of pH 4.6	$2.9 \cdot 10^{-7}$-$1.4 \cdot 10^{-6}$ / $9.5 \cdot 10^{-8}$	[30]
SW ASV	HDME	2,2'-bipyridine + tetraethylammonium perchlorate	$1 \cdot 10^{-8}$-$1 \cdot 10^{-5}$ / $2 \cdot 10^{-8}$	[27]
SW ASV	RD GCE HgBi FE	0.1 M acetate buffer	–	[20]

[a] DCP – direct current polarography, LSP – linear sweep polarography, ACP – alternating current polarography, DPP – differential pulse polarography, LS ASV – linear sweep anodic stripping voltammetry;
[b] DME – dropping mercury electrode, MH DME – micrometer hanging dropping mercury electrode, SMDE – stationary mercury dropping electrode, HDME – hanging dropping mercury electrode, FE – film electrode, MFE on GCE – microfilm electrode on a glassy carbon electrode, RD GCE HgBi FE – rotating disc GCE coated with a film of HgBi amalgam;
[c] analytically useful concentration.

In the absence of complexing agent, low pH is required to avoid formation of gallium hydroxy complexes and to obtain stable peak currents [15-17]. However, a Ga(III) reduction wave was obtained in $NH_3 + NH_4Cl$ or NaOH [11,15,19].

Supporting electrolytes (see Table 1) have been recommended for gallium determination by polarography and ASV in a variety of samples. These techniques are characterized by a wide linear range, even up to 3-4 orders of concentration [27,28]. Polarographic techniques allow determining $n \cdot 10^{-5}$ M of Ga(III), and in the case of DP polarography, down to 10^{-7} M of Ga(III) [28]. ASV is characterized by significantly higher sensitivity, especially in the case of DP mode, where the detection limit is as low as $n \cdot 10^{-11}$ M.

The majority of the polarographic and voltammetric techniques proposed for the determination of Ga are not sufficiently selective. The most common type of interference is the similarity of peak potentials [17]. From this point of view Zn(II) and As(III) have been recognized as potential interferents [14-16,18,29]. In some cases Ga(III) needs to be separated from Mo, Mn, Sn, Ni, Co, and U [14,15,18,29].

However, Ga can be determined in the presence of Al, Fe, and Zn when $KSCN + NH_4Cl$ + tropeolin 00 is used [15], or in the presence of large amounts of Al, Bi, Sn(IV), In, or Cd, when salicylic acid or salicylate is used [14,15,29].

In the medium 0.02 M $NaClO_4$ + 0.005 M CH_3COOH the difference between the peak potentials of Ga and Pb, or Ga and Cd, is sufficient to determine Ga in the presence of a 1000-fold excess of these metals without appreciable error [17]. The overlapping problem of the Zn-Ga system was minimized by scanning the potential to a value at which zinc was completely stripped from the electrode. This procedure allowed determining Ga with no significant error in the presence of a 900-fold excess of zinc [17].

The accuracy of the measurements by ASV is also affected by the formation of intermetallic compounds between Ga and Cu, Zn, or Ni [3,31]. Cofré and Brinck [25] reported that addition of Sb(III) to a Zn-containing electrolyte destroyed the Zn-Ga intermetallic compound by the formation of a Zn-Sb intermetallic compound with a higher formation constant than that of the Zn-Ga compound.

2.2. Use of organic agents

The most suitable medium for voltammetric or polarographic determination of gallium is an organic complexing medium. Several types of ligand containing N and O donors, such as hydroxyazo dyes, triphenylmethane dyes, alizarines, flavonoids, trioxyfluorones and cupferron, *etc.*, have been investigated (Table 2). Ligands containing S donors are rarely used, however, ammonium pyrrolidine dithiocarbamate and diethyldithiocarbamate showed good results.

The Ga(III) complexes formed with the investigated reagents show electrochemical activity. The complexes are reduced or oxidized according to the following main mechanisms: reduction of the elemental species in the adsorbed complex [7,32-34], reduction of the ligand in the adsorbed complex [15,31,35-38], or simultaneous reduction of the elemental species and the ligand in the adsorbed complex [39].

Electrochemically active ligands are of special interest for the determination of Ga(III), which is not easily reduced in conventional supporting electrolytes. The peak corresponding to the reduction of the ligand in Ga(III) chelate is the basis of voltammetric techniques of Ga(III) determination with hydroxyazo dyes [15,31,35-38], alizarin red S [40], and alizarin violet [39].

The reduction of an electrochemically active ligand in the complex can occur *via* two mechanisms:
(1) The complex is reduced, but does not dissociate (a metal ion is bound to the reduced form of the ligand);
(2) The complex dissociates on the surface of the electrode and a free ligand is reduced.

There is little information about the mechanism of ligand reduction in gallium complexes. The mechanism has been studied only for azo dye-Ga(III) complexes, which are reduced by the first mechanism [38] according to [41].

The use of organic ligands allows determination of Ga(III) by polarography with a detection limit down to $n \cdot 10^{-7}$-10^{-8} M. Most Ga complexes are surface-active compounds able to adsorb on the working electrode. This ability is used for the accumulation of analyte on the electrode surface with further oxidation or reduction. AdSV was used for highly sensitive determination of Ga with catechol [7,32], solochrome violet RS [31], alizarin red S [40], morin [34], ammonium pyrrolidine dithiocarbamate, diethyldithio-carbamate, or pyrocatechol violet [3] with a detection limit of down to $n \cdot 10^{-11}$ M.

The selectivity of complex formation significantly enhances the selectivity of Ga determination. The main interferences when using conventional supporting electrolytes are metal ions with redox potentials similar to that of Ga(III), for example Zn(II), Ni(II), and As(III). The problem of Zn interference can be resolved by using solochrome violet RS [31], morin [34], eriochrome red B, and kalces [38]. Good selectivity was obtained using morin [34]. Ga(III) can be determined in presence of large amounts of Ca, Mg, Ni, Cd, Pb, Fe, Al, Zn, and Cu. In [3,7,33,34,38] it was shown that it is possible to determine Ga(III) in the presence of concomitant metal ions such as Fe, Al, Sc, rare-earth elements, and In.

Multielemental analysis by voltammetry is a field of great interest for the future [42]. Simultaneous determination of Ga(III) and Al(III) with mordant red 5 [35], Ge with catechol [7], Ni(II) with solochrome violet RS [31], or Sc(III) with kalces [38] have been reported.

Table 2 Organic agents for voltammetric determination of Ga(III).

Method [a]	Working electrode	Reagent	Linear range /or (and) Detection limit, M	Reference
DCP	DME	catechol	–	[33]
DP AdSV	Hg (Ag) FE	catechol	$1.0 \cdot 10^{-10}$ (preconcentration time 90 c) $1.25 \cdot 10^{-9}$-$9.0 \cdot 10^{-8}$ / $6.5 \cdot 10^{-10}$ (preconcentration time 30 s)	[32] [7]
DCP	DME	eriochrome violet	$1.4 \cdot 10^{-5}$-$1.4 \cdot 10^{-4}$	[15]
DCP	DME	sodium salt of 5-sulfo-2-oxy-α-benzol-azo-2-naphtol	$4 \cdot 10^{-6}$-$2 \cdot 10^{-3}$	[15]
DCP	DME	mordant red 5	$1.0 \cdot 10^{-6}$-$1 \cdot 10^{-3}$	[35]
LSP	DME	acid chrome dark blue	$7.2 \cdot 10^{-7}$-$7.5 \cdot 10^{-6}$	[36]
LS AdSV	SMDE	solochrome violet RS	$1.2 \cdot 10^{-9}$	[31]
DCP	DME	eriochrome blue black R	$1.1 \cdot 10^{-7}$-$8.6 \cdot 10^{-6}$ / $5.7 \cdot 10^{-8}$	[37]
LSP	DME	eriochrome red B	$1.0 \cdot 10^{-7}$-$1.0 \cdot 10^{-5}$ / $2.0 \cdot 10^{-7}$	[38]
		eriochrome black T	$1.0 \cdot 10^{-6}$-$2.0 \cdot 10^{-5}$ / $1.0 \cdot 10^{-6}$	
		calcon	$1.0 \cdot 10^{-6}$-$1.0 \cdot 10^{-5}$ / $1.0 \cdot 10^{-6}$	
		kalces	$1.0 \cdot 10^{-6}$-$2.0 \cdot 10^{-5}$ / $5.0 \cdot 10^{-7}$	
PP	DME	alizarin red S	$7.2 \cdot 10^{-7}$	[43]
CAdSV	CPE	alizarin red S	$2.9 \cdot 10^{-10}$-$8.6 \cdot 10^{-8}$ / $1.4 \cdot 10^{-10}$	[40]
LSP	DME	alizarin violet	$2.0 \cdot 10^{-8}$-$2.0 \cdot 10^{-6}$ / $2.0 \cdot 10^{-8}$	[39]
LS AAdSV	CPE	alizarin complexone	$5.0 \cdot 10^{-10}$-$8.0 \cdot 10^{-7}$ / $3.0 \cdot 10^{-10}$	[44]
LSV	DME	dibromoalizarin violet	$2.9 \cdot 10^{-7}$-$1.0 \cdot 10^{-5}$	[45]
LSV	HDME	salicyl fluorone	$1.5 \cdot 10^{-9}$-$6.0 \cdot 10^{-7}$ / $1.0 \cdot 10^{-9}$	[46,47]
LSV	SMDE	phenylfluorone	$1.4 \cdot 10^{-8}$-$1.0 \cdot 10^{-5}$	[48]
LSP	DME	cupferron	$7.2 \cdot 10^{-8}$-$3.6 \cdot 10^{-8}$	[49]
LSP	DME	4,7-diphenyl-1, 10-phenanthroline	$8.0 \cdot 10^{-8}$-$3.0 \cdot 10^{-6}$ / $7.0 \cdot 10^{-8}$	[50]
DCP	DME	quercetin	$2.9 \cdot 10^{-7}$-$6.9 \cdot 10^{-6}$	[51]
1.5 order differential LSV	HDME	rutin	$1.0 \cdot 10^{-10}$-$1.0 \cdot 10^{-7}$ / $7.5 \cdot 10^{-11}$	[52]
CSV	HDME	morin	$1.4 \cdot 10^{-8}$-$1.7 \cdot 10^{-6}$ / $4.3 \cdot 10^{-9}$	[53]
1.5 derivative LS AdSV	HDME	morin	$1.0 \cdot 10^{-7}$-$1.0 \cdot 10^{-9}$ / $4.0 \cdot 10^{-10}$	[34]
Derivative adsorption chronopotentiometry	HDME	morin	$6.0 \cdot 10^{-11}$	[54]
DP AdSV	HDME	ammonium pyrrolidine dithiocarbamate	$5.0 \cdot 10^{-8}$-$2.7 \cdot 10^{-7}$ / $5.0 \cdot 10^{-8}$	[3]
		diethyldithiocarbamate	$1.0 \cdot 10^{-9}$-$2.1 \cdot 10^{-7}$ / $1.3 \cdot 10^{-9}$	
		pyrocatechol violet	$5.0 \cdot 10^{-9}$-$4.8 \cdot 10^{-7}$ / $9.9 \cdot 10^{-9}$	
DCP	DME	bromopyrogallol red	$1.4 \cdot 10^{-7}$-$1.4 \cdot 10^{-5}$	[55]
DPP	DME	quinolin-8-ol	$1.4 \cdot 10^{-6}$-$7.2 \cdot 10^{-5}$ / $5.7 \cdot 10^{-7}$	[56]

[a] DP AdSV – differential pulse adsorptive stripping voltammetry, LS AdSV – linear sweep adsorptive stripping voltammetry, PP – pulse polarography, CAdSV – cathodic adsorptive stripping voltammetry, LS AAdSV – linear sweep anodic adsorptive stripping voltammetry, LSV – linear sweep voltammetry, CSV – cathodic stripping voltammetry.

3. Other electrochemical methods

3.1. Potentiometry

Ion-selective electrodes have found widespread use for the direct determination of ionic species in complex samples [57,58]. However, only a few electrodes have been developed for Ga(III) ion determination. Some characteristics of the electrodes and developed techniques are presented in Table 3.

Table 3 Characteristics of ion-selective electrodes for Ga(III) determination.

Membrane composition	pH	Concentration range, M	Detection limit, M	Response time, s	Life time, days	Reference
Anion exchange resin – PVC [a]	6 M HCl	$1.0 \cdot 10^{-6}$-$1.0 \cdot 10^{-2}$	–	30	–	[59]
2,9-dimethyl-4,11-diphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene – PVC – dibutylphthalate – sodium tetraphenyl borate	4.0-10.0	$1.45 \cdot 10^{-6}$-0.1	–	12	100	[60]
4-(*p*-nitrophenyl azo)-pyrocatechol – PVC – tributylpho-sphate	3.5	$5 \cdot 10^{-6}$-$8.3 \cdot 10^{-5}$	$4 \cdot 10^{-6}$	600-900	–	[61]
multi-walled carbon nanotube PVC based on 7-(2-hydroxy-5-methoxybenzyl)-5,6,7,8,9,10-hexahydro-2H benzo [b][1,4,7,10,13] dioxa triaza cyclopentadecine-3,11(4H,12H)-dione ionophore + dibutyl sebacate	2.4-6.0	$7.9 \cdot 10^{-7}$-$3.2 \cdot 10^{-2}$	$3.2 \cdot 10^{-7}$	10-16	40	[58]
aliquat 336 – PVC	–	$1.0 \cdot 10^{-4}$-$1.0 \cdot 10^{-1}$	$2.0 \cdot 10^{-5}$	<100	90	[62]
12-crown-4-dibutylphthalate – PVC	3.0-5.0	$1.0 \cdot 10^{-5}$-$3.3 \cdot 10^{-2}$	$7.0 \cdot 10^{-6}$	50-90	57	[63]
2-amino-3-(N-phenylmethyl-2-amino-1,4-naphthoquinonyl)-1,4-naphthoquinone – PVC – potassium tetrakis (4-chlorophenyl borate) – o-nitrophenyloctyl ether	4.3-4.6 3.5-7.4 [b]	$2.3 \cdot 10^{-7}$-$1.2 \cdot 10^{-2}$	$1.2 \cdot 10^{-7}$	11	80	[64]

[a] PVC – poly(vinyl chloride);
[b] in the presence of sodium citrate as inhibitor of Ga(OH)$_3$ formation.

Table 4 Comparison of methods of Ga(III) determination.

Detection limit, M	Method	Reference
	Voltammetric methods	
$5.7 \cdot 10^{-11}$	DP ASV	[17]
$7.5 \cdot 10^{-11}$	1.5-order differential LSV	[52]
$1.0 \cdot 10^{-10}$	DP AdSV	[32]
$1.4 \cdot 10^{-10}$	CAdSV	[40]
$1.2 \cdot 10^{-9}$	LS AdSV	[31]
$1.4 \cdot 10^{-9}$	DP ASV	[26]
$4.3 \cdot 10^{-9}$	CSV	[53]
	Other methods	
$5.0 \cdot 10^{-13}$	ICP MS	[68]
$8.6 \cdot 10^{-9}$	ICP OES	[66]
$7.17 \cdot 10^{-9}$	Spectrofluorimetry	[69]
$8.6 \cdot 10^{-7}$	X-ray fluorescence	[70]
$1.5 \cdot 10^{-8}$	GF AAS	[67]
$4.3 \cdot 10^{-8}$	GF AAS	[71]
$7.3 \cdot 10^{-9}$	Derivative spectrophotometry	[72]
$3.3 \cdot 10^{-7}$	Spectrophotometry	[73]

Table 5 Determination of Ga(III) in industrial and natural objects.

Sample	Reagent or supporting electrolyte	Method	Reference
Bauxite	LiCl	DCP	[15]
Iron, steel	$HClO_4 + NH_4SCN$	ACP	[15]
High-purity aluminum	salicylic acid + NH_4Cl	LS ASV	[29]
Aluminum alloys	alizarin violet	LSP	[39]
Aluminum alloys	salicyl fluorone	LSP	[46,47]
Aluminum samples spiked with Ga	KSCN	DP ASV	[26]
High-purity indium, antimony	sodium salicylate + KCl	LS ASV	[15]
In-Ga alloy	acetate buffer	SW ASV	[20]
Synthetic U-Ga samples	$NaSCN + NaClO_4$	SW ASV	[18]
Sm-Ga, Zn-Ga alloys, luminophore	eriochrome red B, calcon, kalces	LSP	[38]
Standard alloys	quinolin-8-ol	DPP	[56]
Reagent, crystal and saturated liquor of KH_2PO_4	morin	Derivative adsorption chronopotentiometry	[54]
GaAs, Si-Al alloys	–	Direct potentiometry	[59]
Ni alloy, fly ash, aquatic plant	–	Direct potentiometry	[60]
Steels, irons, ores and slags	morin	CSV	[53]
Rocks	2,2'-bipyridine	SW ASV	[27]
Rocks and soils	bromopyrogallol red	DCP	[55]
Ores	acid chrome dark blue	LSP	[36]
Ores	eriochrome blue black R	DCP	[37]
Ores	quercetin	DCP	[51]
Industrial waste water, fly ash	acetate buffer	DPP	[28]
Water spiked with Ga	buffer solution of pH 4.6	SW ASV	[30]
Water and soil samples spiked with Ga	cathechol	DP AdSV	[7]
Coastal sea and rain water	solochrome violet RS	LS AdSV	[31]
Certificate water sample, tap water sample spiked with Ga	diethyldithiocarbamate	DP AdSV	[3]
River water sample spiked with Ga	-	Direct potentiometry	[58]
Food	alizarin red S	CAdSV	[40]
Food	alizarin complexone	LS AAdSV	[44]
Food	4,7 -diphenyl -1, 10 –phenanthroline	LSP	[50]
Grain	rutin	1.5 order differential LSP	[52]
Wheat and maize flour, millet, rice	morin	1.5 derivative LS AdSV	[34]
Peach and tomato leaves, river sediments, coal fly ash	-	Direct potentiometry	[64]

3.2. Coulometry

Only one work related to coulometric determination of Ga(III) has been reported [65]. Milligram levels of gallium were determined by controlled potential coulometry in a medium of 4 M $NaClO_4$ + 0.5 M NaSCN, employing stirring mercury as a working electrode.

Conclusions

Voltammetric methods are the most developed and common for gallium determination among the electrochemical methods. They are used since the 1950-60s. Other electroanalytical methods have been studied, but are rarely used. However, recently several articles dealing with the application of ion-selective electrodes for Ga(III) quantitation have appeared. As to coulometry, only one technique has been presented.

Different investigations have shown the advantages of the electroanalytical methods with respect to other methods for the determination of gallium. Significant attention was paid to voltammetry as the most widely used method for gallium determination. First of all, voltammetric techniques do not need expensive and sophisticated instrumentation. In addition, the process of formation of electrochemically active species is fast and, in the majority of cases, occurs at room temperature, which ensures rapid determination. These features are the

main advantages with respect to inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma optical mass spectrometry (ICP MS), or atomic absorption spectrometry, where much time is required to find an appropriate chemical modifier or reference element, and instrumentation is not available in all laboratories [66,67].

The selectivity of the voltammetric methods for the determination of Ga is not sufficient when conventional supporting electrolytes are used. However, the ability of Ga(III) to form complexes with organic agents of different nature have allowed improving the selectivity of its determination by voltammetry or potentiometry and even multielemental analysis is possible [7,31,35,38]. Gallium can be determined in the presence of Al or Zn, which accompany Ga(III) in natural objects. This is a very positive point since the determination of Ga by ICP OES in the presence of Al is complicated because aluminum in high concentrations interfers strongly [66] and in some cases separation techniques are required.

Voltammetric and potentiometric techniques are characterized by a wide linear range of Ga(III) concentrations, especially potentiometry. When ion-selective electrodes are used, Ga(III) can be determined in the range of 10^{-7}-10^{-2} M. Voltammetry and potentiometry possess sufficient sensitivity with a detection limit of $n \cdot 10^{-7}$-10^{-8} M. Highly sensitive determination of Ga(III) can be carried out when ASV or AdSV is used. Regards the sensitivity, voltammetry can be compared with other highly sensitive physical methods and predominates over spectroscopic methods (Table 4).

Gallium is the constituent of a variety of real objects. The low detection limit of voltammetry allows determining gallium in such special samples as food, water, or soil (Table 5).

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