Stripping Voltammetry Methods for Rare Earth Elements

Subjects: Chemistry, Analytical

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Rare earth metals are used in the most dynamically developing areas of the high technology industry, such as aviation, space flights, production of mobile phones (smartphones), catalysts, high-energy magnetic materials, LCD screens, LED diodes, hybrid car engines, and new generation Ni-MH batteries. These metals are widely used in metallurgy as alloying additives to improve the properties of doped metals, permanent magnets or polishing pastes. The biological activity of lanthanum compounds has also been proven and, hence, they are used in medicine. They have also found a unique application in the production of optical filters, phosphors, dyes, fertilizers, and insulation fibers. Rare earth elements (REEs) have become indispensable in the world of technology, owing to their unusual magnetic, phosphorescent, and catalytic properties. The growing demand for these elements has resulted in these metals being included in the group of 20 critical mineral raw materials for the EU economy. The main environmental risk posed by rare earth elements is tailings, which are a mixture of small-sized particles, waste water, and floatation chemicals used in the processing stages. Most rare earth elements also consist of radioactive materials which impose the risk of radioactive dust and water emissions.

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1. Adsorption Stripping Voltammetry Procedures of Rare Earth Elements Determination

As already mentioned in the introduction to this research, the adsorption stripping voltammetry (AdSV) method has been widely used for the voltammetric determination of different rare earth elements. To be able to determine elements using this method, they must form stable complexes with an appropriately selected complexing agent. In the form of complexes, these elements adsorb on the electrode surface without undergoing any electrolysis processes. Therefore, the complexing agent used has a huge impact on the signal of the determined elements, and thus on the sensitivity of voltammetric analysis. The complexing agents applied in the voltammetric procedures of REE quantification, including the detection limits achieved in these methods, are presented in **Table 1**. As can be seen, the most frequently selected complexing agent of REEs is Alizarin [1][2][3][4][5]. The following ligands are used less often in adsorptive stripping analysis of lanthanides: Alizarin S [6][7], cupferron [8], mordant red 19 (MR19) [9], mixed complex of 2-thenoyltrifluoroacetone (TTA) and polyethyleneglycol (PAG) [10], o-cresolphthalexon (OCP) [11], and solochrome violet RS (SVRS) [12]. In each of the above procedures, the complexing agent was added directly to the tested sample during the analysis. As regards the other procedures, the role of the complexing agent was played by a modifier that was a component of the working electrode and there was no need to add any ligands to the solution.

Table 1. Analytical performance of voltammetric procedures for rare earth elements determination. The methods were ranked by means of rising limit of detection.

Tested Ion	Method	Working Electrode	Complexing Agent	*LOD* (M)	Accumulation Time (s)	Peak Potential *Ep* (V)	Linear Range (M)	Investigated Interferents			Ref.
								Foreign Ions (Other Than REEs)/Organics: Interfering	Foreign Ions (Other Than REEs)/Organics: No Interfering	REEs: Interfering/No Interfering	
La(III)	AdSV	MBTH/CPE	-	1.0 × 10^{-12}	-	−0.22 (vs. Ag/AgCl, 3 M KCl)	1.0 × 10^{-12}–7.0 × 10^{-11}	-	Al(III), Ba(II), Cu(II)	-/ Ce(III)	[13]
Ce(III)	AdSV	Ce-IIM/PC/GCE	-	1.0 × 10^{-12}	600	0.88 (vs. Ag/AgCl, 3 M KCl)	3.0 × 10^{-12}–1.0 × 10^{-4}	Cu(II), Fe(III), Ni(II)	Co(II), Mg(II), Na(I), Zn(II)	-/ Dy(III), Er(III), Eu(III), Gd(III), Ho(III), Nd(III), Pr(III), Tb(III), Yb(III)	[14]
Ce(III)	AdSV	Ce-IP/MWCNT/CPE	-	1.0 × 10^{-11}	-	1.05 (vs. Ag/AgCl, 3 M KCl)	2.5 × 10^{-11}–1.0 × 10^{-6}	-	Ag(I), Cr(III), Cd(II), Co(II), Hg(II)	Dy(III), Eu(III) / La(III), Nd(III), Sm(III), Tb(III), Yb(III)	[15]
Eu(III)	AdSV	HMDE	Cupferron	6.0 × 10^{-11}	60	−0.88 (vs. Ag/AgCl, 3 M KCl)	0–1.3 × 10^{-8}	Cr(III)	Al(III), Mo(VI), U(VI), V(V)	-/ Dy(III), Er(III), Eu(III), Gd(III), Ho(III), Nd(III), Pr(III), Sm(III), Tb(III), Yb(III)	[8]
Dy(III) Ho(III) Er(III) Tm(III) Yb(III) Lu(III)	AdSV	CPE	Alizarin	1.0 × 10^{-10}	60	0.586 0.588 0.588 0.584 0.582 0.580	1.0 × 10^{-9}–2.0 × 10^{-7}	Co(II), Cu(II), Ni(II), Pb(II), Zn(II)	Ca(II), Ba(II), Cr(III), Se(IV), B(III), Ge(IV), As(III), Ag(I), Mn(II),Mg(II),Cd(II), Al(III), V(V), Hg(II),	-/ La(III), Ce(III), Pr(III), Nd(III), Sc(III)	[4]

Tested Ion	Method	Working Electrode	Complexing Agent	*LOD* (M)	Accumulation Time (s)	Peak Potential *Ep* (V)	Linear Range (M)	Investigated Interferents			Ref.
								Foreign Ions (Other Than REEs)/Organics: Interfering	Foreign Ions (Other Than REEs)/Organics: No Interfering	REEs: Interfering/No Interfering	
						(vs. SCE)			Ti(IV), Sb(III), Sn(IV), Fe(II), Ga(III), Fe(III), Th(IV), Zr(IV), In(III), SO_4^{2-}, PO_4^{3-}, F^-		
La(III) Ce(III) Pr(III)	AdSV	SMDE	OCP	1.2×10^{-10} 1.7×10^{-10} 1.4×10^{-10}	1200	−0.95 −1.00 −1.05 (vs. Ag/AgCl, 3 M KCl)	2.5×10^{-9}–2.5×10^{-8}	gelatin, albumin	Ca(II), Mg(II), Al(III), Cu(II), Cd(II), Hg(II), Zn(II), cholesterol, chloride	no data	[11]
Ce(III)	AdSV	PC/GCE	-	2.0×10^{-10}	10	0.85 (vs. Ag/AgCl, 3 M KCl)	2.0×10^{-9}–1.0×10^{-7}	Al(III), Bi(III)	Zn(II), Cu(II), Pb(II), Cd(II), Hg(II), Tl(I), Re(II), Sb(III), Ge(IV),Te(IV), Se(IV), Ag(I), Au(I), Sn(IV), Co(II)	no data	[16]
La(III) Ce(III) Pr(III)	AdSV	GC/SbFE	Alizarin	3.0×10^{-9} 4.3×10^{-10} 5.0×10^{-9}	360	0.74 0.76 0.79 (vs. Ag/AgCl, 3 M KCl)	7.1×10^{-9}–1.8×10^{-7}	-	Co(II), Fe(II), Mn(II), Ni(II), Pb(II), Zn(II)	La(III)/-	[17]
Ce(IV) Gd(III)	AdSV	DIIP@MNPs/SPCE	-	5.0×10^{-10} 1.2×10^{-9}	180	0.05 −0.37 (vs. Ag/AgCl, 3 M KCl)	1.9×10^{-9}–3.8×10^{-8} 4.6×10^{-9}–5.5×10^{-8}	-	Cr(III), As(III), Ca(II), Mg(II), Al(III), Fe(III), SO_4^{2-}, PO_4^{3-}, ascorbic acid	-/ Dy(III), Ho(III), Nd(III), Pr(III), Y(III)	[18]
La(III) Tb(III) Yb(III)	AdSV	SMDE	MR19	8.0×10^{-10} 5.0×10^{-10} 5.0×10^{-10}	60	−0.682 −0.754 −0.784 (vs. Ag/AgCl, 3 M KCl)	1.0×10^{-8}–1.0×10^{-6}	no data			[9]

Tested Ion	**Method**	**Working Electrode**	**Complexing Agent**	***LOD* (M)**	**Accumulation Time (s)**	**Peak Potential *Ep* (V)**	**Linear Range (M)**	**Investigated Interferents**			**Ref.**
								Foreign Ions (Other Than REEs)/Organics: Interfering	**Foreign Ions (Other Than REEs)/Organics: No Interfering**	**REEs: Interfering/No Interfering**	
Y(III) Dy(III) Ho(III) Yb(III)	AdSV	HMDE	SVRS	1.4×10^{-9} 1.1×10^{-9} 1.0×10^{-9} 5.0×10^{-10}	180	−0.98 −0.98 −1.00 −1.00 (vs. Ag/AgCl, 3 M KCl)	$0–3.4 \times 10^{-7}$ $0–2.5. \times 10^{-7}$ $0–1.8 \times 10^{-7}$ $0–2.3 \times 10^{-7}$	no data			[12]
Ce(III)	AdSV	CTAB/CPE	Alizarin	6.0×10^{-10}	120	0.73 (vs. SCE)	8.0×10^{-10}–8.0×10^{-9}	-	Ca(II), Ba(II), B(III), As(III), Mg(II), Se(IV), Ge(IV), Mn(II), Zn(II), Cr(III), Ni(II), Hg(II), Cd(II), Co(II), Fe(II), Pb(II), Cu(II), Al(III), Bi(III), Fe(III), Zr(IV), In(III), Ga(III), $HCr_2O_7^-$, MnO_4^-, $AuCl_4^-$, SO_4^{2-}, PO_4^{3-}, F^-, ascorbic acid	-/ La(III), Pr(III), Nd(III), Sm(III), Eu(III), Y(III), Gd(III), Tb(III), Sc(III), Dy(III), Ho(III), Er(III), Yb(III), Tm(III)	[2]
Sc(III)	AdSV	CPE	Alizarin	6.0×10^{-10}	60	−0.60 (vs. SCE)	1.0×10^{-9}–6.0×10^{-7}	F^-, $C_2O_4^{2-}$, citrate	Ca(II), Mg(II), Zn(II), Cd(II), Mn(II), Ag(I), As(III), Au(III), Ba(II), Co(II), Cr(III), Hg(II), Ni(II); MoO_4^{2-}, Pb(II), Al(III), Sn(II), Ga(III) Cu(II), Fe(III), Sb(III), V(V), In(III); Bi(III), Th(IV), Zr(IV), Ti(IV), SO_4^{2-}, PO_4^{3-}	-/ Ce(III), Dy(III), Er(III), Eu(III), Gd(III), Ho(III), La(III), Nd(III), Pr(III), Tb(III), Yb(III)	[5]
Sc(III)	AdSV	CPE	Alizarin S	6.0×10^{-10}	180	−0.58 (vs. SCE)	1.0×10^{-9}–4.0×10^{-7}	Fe(III), Zr(IV)	Zn(II), Pb(II), Ni(II), Li(I), Co(II), Mn(II), Cr(III), As(III), Se(IV), Ag(I),	Eu(III), Gd(III), Tb(III), Dy(III),	[7]

Tested Ion	Method	Working Electrode	Complexing Agent	*LOD* (M)	Accumulation Time (s)	Peak Potential *Ep* (V)	Linear Range (M)	Investigated Interferents: Foreign Ions (Other Than REEs)/Organics: Interfering	Investigated Interferents: Foreign Ions (Other Than REEs)/Organics: No Interfering	Investigated Interferents: REEs: Interfering/No Interfering	Ref.
									Au(III), Be(II), Bi(III), Cd(II), Ga(III), Fe(II), Mo(VI), Sn(II), Cu(II), Ba(II), V(V), CNS$^-$, SO$_4^{2-}$, PO$_4^{3-}$, F$^-$, CN$^-$	Ho(III), Er(III), Tm(III), Yb(III), Lu(III) / La(III), Ce(III), Pr(III), Nd(III), Sm(III)	
Ce(III)	AdSV	NHMF/CPE	-	8.0×10^{-10}	350	0.55 (vs. Ag/AgCl, 3 M KCl)	5.0×10^{-9}–9.0×10^{-8}	-	Cd(II), Cr(III), Cu(II), Mn(II), Ni(II), Pb(II), Th(IV), Zn(II), Br$^-$, Cl$^-$, SO$_4^{2-}$, CH$_3$COO$^-$, UO$_2^{2+}$	La(III), Sm(III) / Er(III), Ho(III)	[19]
Ce(III)	AdSV	CPE	Alizarin	2.0×10^{-9}	120	0.69 (vs. SCE)	6.0×10^{-9}–3.0×10^{-7}	Th(IV)	Ba(II), Ca(II), Cr(III), Mg(II), As(III), Se(IV), B(III), Ge(IV), Mn(II), Cd(II), Pb(II), In(III) Co(II), Zn(II), V(V), Hg(II), Fe(III), Fe(II), Ni(II), Sn(IV), Sb(III), Ti(IV), Al(III), Zr(IV), Cu(II), Bi(III) Ga(III), SO$_4^{2-}$, PO$_4^{3-}$, ascorbic acid	-/ La(III), Pr(III), Nd(III), Sm(III), Eu(III), Y(III), Gd(III), Tb(III), Sc(III), Dy(III), Ho(III), Er(III), Yb(III), Tm(III)	[1]
Lu(III)	ASV	HMDE	-	2.1×10^{-9}	120	−0.995 (vs. Ag/AgCl, 3 M KCl)	2.1×10^{-9}–7.3×10^{-6}		no data		[20]
Ce(III)	AdSV	DPNSG/CPE	-	2.3×10^{-9}	600	0.27 (vs. Ag/AgCl, 3 M KCl)	2.30×10^{-9}–6.45×10^{-8}	-	Cd(II), Cr(III), Mn(II), Ni(II), Pb(II), Th(IV), Zn(II), Br$^-$, Cl$^-$,	La(III) / Er(III), Ho(III), Sm(III)	[21]

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It can be noted that depending on the developed procedure, the use of Alizarin as a complexing agent enables the determination of light or heavy rare earth elements. For example, the procedure [4] developed using Alizarin is more sensitive to heavy rare earths (Dy, Ho, Er, Tm, Yb, and Lu) than to light ones. The procedure [5] is dedicated to the determination of scandium only, whilst both methods [1][2] are suitable for the detection of cerium. In all the above-mentioned procedures, the CPE was used as the working electrode. However, in the work [17], the GCE/SBF sensor gave the best voltammetric response to cerium, whilst the responses to lanthanum and praseodymium were lower. Because of a significant variance between the peak potentials of Ce(III)-Alizarin and other rare earth(III)-Alizarin complexes, Alizarin is the most often used to determine cerium individually in the presence of other rare earths. The use of mordant red 19 (MR19) as a complexing agent in the paper [9] allowed indirect analysis of both light and heavy lanthanide ions and even simultaneous determination in certain lanthanide mixtures. Despite the similar chemical properties of all lanthanides, the MRl9 complex system used in this research can differentiate between light lanthanide ions and heavy ones because the variance in peak potentials between the lanthanide-MR19 complex and free MR19 increases with the increase in the atomic number of the lanthanide ion. To be exact,

Tested Ion	Method	Working Electrode	Complexing Agent [9]	*LOD* (M)	Accumulation Time (s)	Peak Potential *Ep* (V)	Linear Range (M)	Investigated Interferents: Foreign Ions (Other Than REEs)/Organics: Interfering	Investigated Interferents: Foreign Ions (Other Than REEs)/Organics: No Interfering	Investigated Interferents: REEs: Interfering/No Interfering	Ref.
									CH_3COO^-, SO_4^{2-}, UO_2^{2+},		
Ce(III)	CSV	[11] ITO electrode	-	5.8 × 10^{-9}	300	0.55 (vs. Ag/AgCl, 3 M KCl)	1.0 × 10^{-7}–7.0 × 10^{-7}	Mn(II)	Bi(III), Cu(II), Zn(II), Sn(II), Mg(II)	-/ Eu(III)	[22]
Eu(III)	AdSV	SDBS/LaB_6 electrode	-	6.0 × 10^{-9}	120 [12]	−0.70 (vs. SCE)	1.0 × 10^{-8}–2.0 × 10^{-6}	Fe(II), Mg(II), Mn(II), Pb(II), SDBS, SDS, CTAB	Na(I), Ca(II), Zn(II), Triton X-100, CPB	Ce(III), Er(III), La(III) / Sm(III), Yb(III)	[3]
Yb(III)	AdSV	HMDE	TTA-PAG ligand	-	[4][9][11][12][17] 180	1.65 (vs. Ag/AgCl, 3 M KCl)	5.0 × 10^{-9}–1.0 × 10^{-7}	-	Cr(III), Co(II), Mn(II), Mo(VI), U(VI), V(V), Triton X-100	-/ Eu(III), La(III), Y(III)	[10]
Eu(III)	AdSV	N/MWCNTs/GCE	-	1.0 × 10^{-8}	60	−0.70 (vs. SCE)	4.0 × 10^{-8}–1.0 × 10^{-4}	Bi(III), Cr(III)	Mn(II), Co(II), Pd(II), Mg(II), Zn(II), Fe(II), Ba(II), Ni(II) [10]	Er(III), La(III), Sm(III), Yb(III) /-	[23]
Eu(III)	AdSV	Sal-SAMMS/SPCE	-	1.0 × 10^{-8}	300	−0.75 (vs. Ag/AgCl, 3 M KCl)	7.5 × 10^{-8}–5.0 × 10^{-7}	no data			[24]
Eu(III) Yb(III)	AdSV	NCTMFE	-	3.0 × 10^{-8} 2.0 × 10^{-8}	300	−0.62 −1.46 (vs. SCE)	X–2.0 × 10^{-6} [21]	no data		La(III)/no data	[25]
Ce(III)	AdSV [19] [27]	GCE	Alizarin S [28] [13]	6.0 × 10^{-8}	30	0.60 (vs. Ag/AgCl, 3 M KCl)	[18] 2.0 × 10^{-7}–8.0 × 10^{-6} [14][16][26] [29]	Cr(III), Fe(II), Sb(III), V(V)	Al(III), As(III), As(V), Cd(II), Co(II), Cr(VI), Hg(II), K(I), Mg(II), Mn(II), Na(I), Ni(II) [24] Pt(IV), Se(IV), Se(VI), Sn(II), Ti(IV), U(VI), Zn(II), Bi(III), Ga(III), Cu(II), Mo(VI),	no data [14]	[6]

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On the other hand, no complexing agent was used in the AdSV procedure described in the works [3][23][25]. Instead of this, ion-exchange preconcentration of both europium and iterbium on Nafion-coated thin mercury film electrodes (NCTMFE) was proposed in the work [25]. However, in the method [23], as a result of the exchange of Eu(III) by Nafion and subsequent electrostatic adsorption on the surface of the multiwall carbon nanotubes film (MWCNTs), the maximum Eu(III) incorporation into the composite film is achieved. In the work [3], the electrostatic adsorption of Eu(III) on a monolayer of a surfactant such as sodium dodecylbenzene sulfonate (SDBS), formed on the surface of the LaB6 electrode, was also reported.

2. Anodic Stripping Voltammetry Procedure for Lutetium(III) Determination

Kumric et al. described an indirect anodic stripping voltammetry procedure for Lu(III) quantification, based on the substitution reaction between Lu(III) and Zn-EDTA. Since the reduction potential of Lu(III) at a mercury electrode is greatly negative, close to the decomposition potential of the supporting electrolyte, direct determination of Lu(III) by

Tested Ion	Method	Working Electrode	Complexing Agent	*LOD* (M)	Accumulation Time (s)	Peak Potential *Ep* (V)	Linear Range (M)	Investigated Interferents			Ref.
								Foreign Ions (Other Than REEs)/Organics: Interfering	Foreign Ions (Other Than REEs)/Organics: No Interfering	REEs: Interfering/No Interfering	
									CTAB, rhamnolipid, humic acid, Triton X-100, SDS, fulvic acid, natural organic matter		
Eu(III)	AdSV	IIM/PC/SPE	-	1.0 × 10^{-7}	300	−1.00 (vs. Ag/AgCl, 3 M KCl)	3.0 × 10^{-7}–1.0 × 10^{-3}	-	Ca(II), Co(II), Cu(II), Fe(III), Mg(II), Na(I), Ni(II), Zn(II)	-/ Dy(III), Er(III), Ce(III), Gd(III), Ho(III), Nd(III), Pr(III), Tb(III), Yb(III)	[26]
Eu(III)	AdSV	IIPs-CPE	-	1.5 × 10^{-7}	20	−0.18 (vs. Ag/AgCl, 3 M KCl)	5.0 × 10^{-7}–3.0 × 10^{-5}	Cd(II), Cu(II)	Ag(I), Ca(II), Hg(II), Mg(II), Pt(II), Zn(II)	Ce(III), Gd(III), Sm(III) / Er(III), Dy(III), La(III)	[27]
Ce(III)	AdSV	IIPs-CPE	-	1.5 × 10^{-7}	20	0.93 (vs. Ag/AgCl, 3 M KCl)	1.0 × 10^{-6}–1.0 × 10^{-5}	no data		-/ Dy(III), Er(III), Eu(III), Gd(III), Ho(III), Nd(III), Pr(III), Tb(III), Yb(III)	[28]
Eu(III)	AdSV	PO/GE	-	3.0 × 10^{-7}	-	1.10 (vs. Ag/AgCl, 3 M KCl)	1.0 × 10^{-6}–8.0 × 10^{-5}	-	Al(III), Fe(III)	no data	[29]

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4. Types of Working Electrodes and Electrode Modifiers Used

4.1. Mercury-Based Electrodes

Up to 2000, voltammetric methods were most often based on the use of mercury electrodes characterized by excellent adsorption properties, ideal polarizability, smooth surface, good signal repeatability, and a wide range of negative potential values. Unfortunately, due to the ease of metal oxidation, mercury electrodes have a relatively limited application in the anode area. In voltammetric determination of trace amounts of rare earth elements, mercury electrodes, such as the hanging mercury drop electrode (HMDE) [8][10][12][20], the static mercury drop electrode (SMDE) [9][11], and the Nafion-coated thin mercury film electrode (NCTMFE) [25], have been used. Both the HMDE and SMDE are mercury electrodes with a special design that enables the voltammetric process to be carried out on one drop of mercury. A great convenience in using mercury drop electrodes is that there is no need to specially prepare their surface, and what is more, it is renewed periodically so no contamination accumulates on them. Nevertheless, this electrode structure does not allow for a large stirring speed for fear of detaching the drops, and the peaks in the voltammogram recorded using it are slightly wider and lower than those obtained using a mercury film electrode (the time of diffusive metal transport during electrolytic dissolution is longer in the case of

AdSV—Adsorptive stripping voltammetry, CPE—Carbon Paste Electrode, MBTH—3-Methyl-2-hydrazinobenzothiazole, GCE—Glassy carbon electrode, Ce-IIM—cerium ion-imprinted membrane, PC—poly-catechol, Ce-IP—cerium-imprinted polymer, MWCNT—multiwall carbon nanotubes, HMDE—Hanging Mercury Drop Electrode, SMDE—Static Mercury Drop Electrode, OCP—o-cresolphthalexon, GC/SbFE—Glassy carbon antimony film electrode, ASV—Anodic stripping voltammetry, DIIP@MNPs/SPCE—Screen-printed carbon electrode modified with double ion-imprinted polymer @ magnetic nanoparticles, MR19—Mordant Red 19, SVRS—

Solochrome Violet RS, CTAB—Cetyltrimethylammonium bromide, NHMF—N′-[(2-hydroxyphenyl)methylidene]-2-furohydrazide, DPNSG—dipyridyl-functionalized nanoporous silica gel, CSV—Cathodic stripping voltammetry, ITO—Indium tin oxide, SDBS/LaB$_6$—surfactant based on the lanthanum hexaboride and sodium dodecylbenzene sulfonate, TTA-PAC—ligand-mixed complex of 2-thenoyltrifluoroacetone and polyethylene glycol, MWCNTs—multiwall carbon nanotubes and Nafion composite film, Sal-SAMMS/SPCE—Screen-printed carbon electrode modified with salicylamide self-assembled monolayers on mesoporous silica, NCTMFE—Nafion-coated thin mercury film electrode, IIM/PC/SPE—Screen-printed electrode modified with ion-imprinted membrane and poly-catechol, IIPs—ion-imprinted polymers, PO/GE—gold electrode modified with 2-pyridinol-1-oxide, SCE—saturated calomel electrode.

drops than in the case of a film). However, the use of mercury electrodes due to the release of toxic mercury into the environment. The growing risks associated with the use, handling, and disposal of mercury and its salts required for mercury film manufacture restrict the usage in laboratory practice. Therefore, there is an attempt to search for new materials that would allow obtaining electrodes that would have the advantages of mercury electrodes and at the same time would be less toxic.

The first work on the determination of lanthanides using the AdSV method was published in 1985. Wang et al. attempted to determine light lanthanides such as lanthanum, cerium, and praseodymium using an SMDE electrode [11]. A slightly more frequently selected electrode for the determination of REEs has been the HMDE. Using this electrode, the AdSV procedures for Eu(III) [8], Yb(III) [10], Lu(III) [20] as well as Y(IIII), Dy(III), Ho(III), and Yb(III) [12] determination have been developed. The lowest detection limit of 1.6×10^{-11} M was obtained in the procedure of Eu(III) determination based on the complexation of Eu(III) with cupferron. Another mercury electrode used to determine Eu(III) and Yb(III) was a Nafion-coated thin mercury film electrode (NCTMFE) [25].

4.2. Solid Electrodes

An alternative to mercury electrodes is solid electrodes. Frequently used solid electrodes are those made of noble metals (Pt, Au, Ag) or carbon electrodes (glassy carbon, graphite, paste electrode). Unlike mercury electrodes, the above-mentioned electrodes are non-toxic and can be used at both negative and positive potentials. Their use makes it possible to determine ions present in the sample as a result of their reduction or oxidation process. These electrodes are highly stable in various solvents. Additionally, they can be easily prepared as well as chemically modified. Among solid electrodes, only carbon paste electrodes are characterized by a renewable surface. For the other carbon electrodes, as well as the noble metal-based ones, the surface can be renewed only after time-consuming mechanical and electrochemical treatments.

Solid electrodes for the determination of REEs include carbon-based electrodes, such as glassy carbon electrodes (GCEs) [6][14][16][17][23], carbon paste electrodes (CPEs) [1][2][4][5][7][13][15][19][21][27][28] and to a lesser extent gold electrodes [29]. Looking through the literature, it can be safely stated that at the end of the 20th century both GC and CP electrodes, with chemical modifications, received growing importance in the analysis of trace elements, including lanthanides, particularly when used coupled with stripping analysis. The modifier, selected to have high propinquity for the analyte, provides increased selectivity combined with high sensitivity, emerging in the non-electrolytic pre-concentration stage prior to voltammetric analysis [30][31]. Glassy carbon electrodes (GCEs) are generally used as a substrate for film electrodes. In voltammetric determination of REEs, glassy carbon has been used as a substrate for poly(catechol) film [16], poly(catechol) and ion-imprinted membrane [14], antimony film [17], as well as multiwall carbon nanotubes and Nafion composite film [23]. On the other hand, carbon paste electrodes made of graphite grains mixed with a nonconductive oily organic liquid can be easily modified by incorporating a variety of ligands into the paste. Therefore, in several procedures of REE quantification working electrodes were based on a modified carbon electrode [2][13][15][19][21][27][28]. In the latter works, the carbon paste electrode was modified by using cetyltrimethylammonium bromide [2], dipyridyl-functionalized nanoporous silica gel [21], N′-[(2-

hydroxyphenyl)methylidene]-2-furohydrazide (NHMF) [19], cerium-imprinted polymer and multiwalled carbon nanotubes [15], ion-imprinted polymers [27][28] and 3-Methyl-2-hydrazinobenzothiazole (MBTH) [13].

In accordance with the data in **Table 1**, the most sensitive (*LOD* = 1×10^{-12} M) and highly selective AdSV method for the determination of lanthanides was obtained in the work [13], in which MBTH was used as the CPE modifier. This organic ligand containing in its structure an N- and S-based complexing center is capable of selectively coordinating with transition and heavy metals [32]. As described in the article [13], it also forms stable complexes with lanthanum. Javanbakht et al. developed two AdSV procedures for cerium determination using a CPE electrode modified with organic ligands, such as dipyridyl (DP) [21] and NHMF [19], and which directly coordinated with cerium(III). DP forms a complex with Ce(III) through two nitrogen atoms of the pyridine ring, while NHMF coordinates with Ce(III) via donor oxygen and nitrogen atoms.

Both methods can be used to determine cerium concentrations in the range of 10^{-9}–10^{-8} M, but a slightly lower detection limit of 8×10^{-10} M was obtained in the procedure [19]. On the other hand, in the paper [29] on determining europium, 2-pyridinol-1-oxide (PO) was used as a modifier of a gold electrode. The applied organic ligand forms coordination bonds with europium through two oxygen atoms. According to **Table 1**, this method is characterized by the highest detection limit (equal to 3×10^{-7} M) of all voltammetric methods dedicated to lanthanide quantification.

Recently, modified screen-printed electrodes have also been used for REE analysis [18][24][26]. The following materials have been used as modifiers: double-ion imprinted polymer @ magnetic nanoparticles [18], ion-imprinted membrane and poly(catechol) [26], and salicylamide self-assembled monolayers on mesoporous silica [24]. Screen-printed electrodes (SPEs) have currently drawn considerable attention due to several advantages of these sensors such as low cost, high repeatability of the obtained electrodes, flexibility of their design, the possibility of producing them from various materials, and wide possibilities of modification of the working surface. In addition, these electrodes can be connected to portable equipment enabling in situ quantification of specific analytes. Moreover, SPEs often do not need electrode pretreatment or electrodeposition and/or electrode polishing, dissimilar to other electrode materials [33].

Carbon nanotubes are a popular electrode material and they have been applied as a modifier for both CP [15] and GC electrodes [23] due to their distinctive electronic structure, electrical conductivity, large specific surface area, as well as strong adsorption capacity [34]. By using MWCNTs-Nafion film to modify a GCE, the sensitivity of Eu(III) determination was improved because of the catalytical action of MWCNTs and Nafion film’s capacity to accumulate cations. This procedure is characterized by a limit of detection equal to 1×10^{-8} M. Over the last few years, special attention has been attracted to ion-imprinted polymers (IIPs)/membrane (IIM) that have the ability to recognize specific lanthanide ions. Generally, ion-imprinted material is characterized by great selective appreciation, stability, reusability, simplicity, and low cost in preparation. As mentioned earlier, this modifier has been used in as many as six voltammetric methods of lanthanide detection [14][15][18][26][27][28]. The researchers have reported that the imprinted materials can most often be incorporated into carbon paste electrodes, which allows for the development of highly selective sensors for the determination of different kinds of molecules or ions. The development of imprinted materials for lanthanide ions is of particular importance due to the widely known issue of separation of lanthanide ions [35][36][37]. In 2015, scientists from the Banaras Hindu University in India managed to successfully prepare an electrochemical sensor for the simultaneous determination of two lanthanide ions, Ce(IV) and Gd(III), via a dual ion-imprinting approach. The proposed sensor was found to be highly selective and sensitive for the simultaneous quantification of Ce(IV) and Gd(III). The detection limits obtained were 5.0×10^{-10} M and 1.2×10^{-9} M for cerium and gadolinium, respectively [18]. The presence of both multiwalled carbon nanotubes and Ce(III) imprinted polymer nanoparticles in the carbon paste electrode composition allowed a group of researchers led by Alizabeth to obtain a sensor with a low detection limit equal to 1.0×10^{-11} M [15]. Applied in the work [16], a glassy carbon electrode modified with poly(catechol) (PC-GCE) shows a cerium detection limit of 2.0×10^{-10} M, whereas using a poly(catechol) film modified glassy carbon electrode (PC-GCE) additionally modified with Ce(III) ion-imprinted membrane (IIM), it is possible to obtain a much lower detection limit equal to 1.0×10^{-12} M [14]. It has been confirmed that due to the presence of ion-imprinted sites created in ion-imprinted polymers, the electrochemical active surface is larger, and, therefore, a larger amount of the analyte is able to adsorb on the electrode surface. As for procedures in which the working electrodes were modified with poly(catechol), a significant enhancement of the voltammetric response was noticed due to the fact that poly(catechol) forms coordination bonds with lanthanides [14][16][26].

By analyzing the data collected in **Table 1**, it can be concluded that the voltammetric methods using carbon-based electrodes chemically modified with two different modifiers are characterized by wide linearity ranges covering 4 [23][26], 5 [15] or even 8 orders of magnitude [14].

A novelty in the voltammetric determination of REEs has been the use of indium tin oxide (ITO) working electrode material for the determination of cerium by CSV. This electrode is particularly suitable for CSV determinations due to its excellent positive potential range as well as a smooth background current related to metal electrodes such as platinum and gold which have interfering oxide waves. Additionally, the use of an ITO electrode does not require a complicated surface modification process [22]. Another novelty electrode material is lanthanum hexaboride (LaB_6), which was used to determine europium in combination with sodium dodecylbenzene sulfonate as an ionic surfactant [3].

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