

METHODS OF CHEMICAL ANALYSIS

DEVELOPMENT OF POLAROGRAPHIC ANALYSIS OF INORGANIC SUBSTANCES (REVIEW)

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Reviews have recently been published on the theory and apparatus of polarography [1], on polarography in molten salts [2], and on general matters concerning polarography [3]. Data from the literature on methods for determination of individual elements are given in Table 1. A short account follows of some rapidly developing aspects of polarography.

Methods for Increasing Sensitivity

The majority of the investigations in recent years relate to the search for methods of increasing the sensitivity of polarographic analysis. A new method has been proposed for determining very small concentrations of elements by means of their radioactive isotopes. This method [82] involves measurements of the radioactivity of the drops flowing from the capillary at a certain potential. The curve for the dependence of the radioactivity of the emerging mercury on potential is reminiscent of the shape of the normal polarographic curve, but the determination is more sensitive. Nonradioactive elements can be determined by replacing them with radioactive ones.

The effect of ultrasound on the characteristics of the anodic waves in amalgam polarography has been investigated [83], and it was shown that the sensitivity can be increased by one or two orders of magnitude by this method. In amalgam polarography the anode curves are plotted by the derivative method [84]. The sensitivity is higher, and the preliminary electrolysis is shortened. The limiting concentration of cadmium which can be determined is 6×10^{-11} mole/liter.

The interesting fact has been discovered that the sensitivity of the determination of copper, cadmium, and lead is increased by 10-50 times in polarography of solutions containing a mixture of sulfuric acid, ammonium thiocyanate, and thiourea or urotropine [85].

A series of papers have been devoted to theoretical discussion of possibilities of increasing the sensitivity of amalgam inverse polarography. It was shown [86-91] that correct choice of volume of solution for polarography, dimensions and shape of electrodes, reduction of the effect of capacitor current, and increased sensitivity of recording instruments have substantial importance. The sensitivity which can theoretically be achieved under the most favorable conditions is 10^{-11} and $10^{-12}\%$. With a silver-amalgam electrode, which was studied in detail [92], it was possible by this method [87] to determine zinc ions at a concentration of 10^{-11} - 10^{-12} mole/liter and bismuth ions at 10^{-10} mole/liter [93].

The spectra of Cu, Pb, Zn, In, Tl, Sb, Ga, Ge, Bi, and Cd polarographic peak potentials were investigated in solutions of various electrolytes [94]. The effects of electrolysis potential, the pH of the solution, and other factors on the depth of the anodic peaks of antimony [95], cadmium [96], and germanium [97] have been investigated. Accompanying ions which do not interfere with the determination of germanium may be Zn, Sn, Pb, Cd, Tl, Bi, Ni, Mn, Fe, and Co in considerable excess.

Many methods have been developed for determination of microquantities of elements in high-purity metals and other materials by amalgam inverse polarography: Sb in tin [55], Ge in indium [36], Bi and Sb in germanium [56], Cu in steels [8], Cd in salts [26], Mn [72], Tl in indium [35], and Sb, Bi, and Sn in silicon tetrachloride [98]. Although the sensitivity of the determination of the elements named is high, nevertheless the theoretical limit of sensitivity is not attained in any of these works. An evaluation of the possibility of increasing the sensitivity is given in [99, 100].

By use of polarizing potentials in the form of exponential jumps [101, 102] it was possible to separate the capacitor and diffusion currents in time and increase the sensitivity and speed of the apparatus. An evaluation has been made of the pulse polarography method [103]. Polarography of hot solutions by this method was suggested. This has led to development of a sensitive method for determination of titanium in niobium and tantalum pentoxides and of zinc in indium, gallium, and antimony [104].

TABLE 1. Polarographic Determination and Investigation of the Elements

Abbreviations: ap = amalgam polarography with preliminary accumulation on the mercury drop; cl = classical; dp = derivative; sq = square wave; op = oscillographic; pp = pulse; ac = alternating current; II = interfering ions; AI = accompanying ions, in the presence of which the determination can be carried out; S = sensitivity; MC = method of concentration; MS = method of separation of interfering ions.

Element	Supporting electrolyte	Half-wave potential and type of polarography	Characteristics of method	Material analyzed	Source
Cu	Sodium trihydroxyglutamate, pH = 12	-0.90 cl	Cu determination in presence of Fe (1: 1000), $E_{1/2} = -1.65$	Steels, cast irons, slags	4
	0.1-N. HCl	-0.3 cl	MC: Extraction of diethyldithiocarbamate; S = $10^{-6}\%$	Common salt	5
	HCl and tartrate	-0.25 ac	Cu determination, coprecipitated with nickel dimethylglyoximate	—	6
	Triethanolamine, ethylenediamine, alkali	cl	II: Pd, Cd	Zinc	7
	Triethanolamine, alkali	-0.2	S: $5 \cdot 10^{-4}\%$	Steels	8
	NiSO ₄ and ZnSO ₄	-0.75 ap	Preelectrolysis on graphite electrode	Zinc electrolytes	9
	—	cl	MC: Precipitation with hydrosulfuric acid	Rocks	10
	HCl—NaCl	ap		Sodium chloride	11
	Various electrolytes	op	Decomposition of sample with HCl + H ₂ O ₂	Magnetic materials, ferrites	12
	HNO ₃	cl	MC: Extraction of copper dithizonate	Iron, steels	13
	Triethylenetetraminehexaacetic acid	cl	MS: Te, extraction of bromide	Indium concentrates	14
Ag	Thiourea and H ₂ SO ₄	op	AI: Pb, Zn, Cd, Bi. II: Cu. MS from Cu: precipitation of AgCl	Alloys and ores	15
	HI	cl	Determination in gold		16
		ap	By decrease of sulfur-ion peak		17
Au		ap	By decrease of sulfur-ion peaks		17
Mg	Piperidine, pH = 13	-0.88 cl	From wave of complex with solochrome violet RS	Calcium	122
Ca		cl	From wave for Cd displaced from its oxalate by calcium ions	Plant ash	19
Ba and Sr	Ca (OH) ₂	-1.98	MS of Ca: ion exchange	Calcium salts	20
		-2.17 cl			
Zn	KCl NH ₄ Cl	ap	S: $1.5 \cdot 10^{-8}$ mole/liter	Sea water	21
		-1.1 pp	S: $2 \cdot 10^{-4}$ mole/liter	—	18
		pp	S: $10^{-5}\%$ mole/liter	Indium, gallium, antimony	22
	Thiosalicylic acid, triethanolamine, pyridine	op	Development of method. AI: Cu, Mn, Ni, Fe	Magnetic materials	12

TABLE 1 (continued)

Element	Supporting electrolyte	Half-wave potential and type of polarography	Characteristics of method	Material analyzed	Source
	NH ₄ OH	-0.9, cl	MC: Extraction of zinc diantipyrylmethanethiodanide	Copper concentrate	23
	KOH	sq	Decomposition of sample with HNO ₃ and HCl	Arsenic	24
Cd	NH ₄ OH-NH ₄ Cl	-0.67, cl	MS: Cr-CrO ₂ Cl ₂ , Cu, and Cd thioacetamide, extraction of Cu with neocuproin	Stainless steels	25
	NiSO ₄ and ZnSO ₄	ap	Electrolysis on graphite electrode	Zinc and nickel electrolytes	9
	Solutions of K and Na salts	ap	S: 10 ⁻⁶ %	Potassium, sodium, and ammonium chlorides, nitrates, and thiocyanates	26
Cd	NH ₄ OH	cl	MC: Extraction of cadmium diantipyrylmethane bromide	Copper concentrate	27
	KOH	sq	Decomposition of sample with HNO ₃ + HCl	Arsenic	24
	Triethylenetetraminehexaacetic acid	cl	MS of Te: extraction of bromide	Indium concentrates	14
Hg		ap	From decrease of sulfur-ion peak		17
Al	KNO ₃	-1, 2, cl	From reduction wave of nitrate, catalyzed by Al	Various materials	28
Ga	KCNS and other electrolytes	-0.68, -0.86, ap	Investigation of anodic polarography conditions		29
	NH ₄ OH and glycine, pH = 8	-1, 5, cl	MC and MS. extraction of gallium chloride; II: Cu, Cd, Pb, Sn, Fe, Mn. S = 10 ⁻⁴ %	Ores, metals, minerals	30
Tl	Ammoniacal trilon	-0.8, pp	S = 10 ⁻⁵ %, MC: extraction from chloride solution	Indium	31
	KCl	-0.75, pp	S = 2 · 10 ⁻⁵ mole/liter, platinum microdisk electrode		18
	NaOH	ap	Deposition of Tl(OH) ₃ on graphite electrode	Copper, cadmium, indium compounds	33
	H ₂ SO ₄	-0.45, cl	Polarography of solution of sample	Sodium iodide	32
	KOH	sq	Decomposition of sample with HNO ₃ + HCl	Arsenic	24
		ap	- -	Urine	34
	Triethylenetetraminehexaacetic acid	cl	MS Tl: extraction of bromide	Indium concentrates	14
Tl	Ammonium chloride-Complexone III	-1, 0, ap	MS In: extraction of bromide	Indium	35

TABLE 1 (continued)

Element	Supporting electrolyte	Half-wave potential and type of polarography	Characteristics of method	Material analyzed	Source
Ge	Na_2CO_3 -Complexone III	-0.3, ap	CI: Zn, Sn, Fb, Cd, Tl, Bi, Ni. Mn, Fe, Co, II: Cu, S: $M \times 10^{-10}$ mole/liter	Ores; concentrates	36
	Na_2CO_3 -Complexone III, pH 8-9	cl	MC: volatilization of GeCl_4		37
	Alizarin red	op	Investigation of polarography conditions		38
	Alkaline sodium oxalate solution	-1.8, op	Sample decomposed with HNO_3 + HCl mixture	Semiconductor materials	39
Sn	Hydroxyacids, mercaptopropionic acid	cl	Investigation of polarography conditions		40
	NaOH	-0, 9, -1.1, cl	AI: Cl^- , As, Bi, Cu, Pb Reduction of Sn with borohydride		41
Pb	3-N HCl	-0.45, op	Sample dissolved in mercury and Pb extracted by treatment with Bi^{3+} , $S = 2 \cdot 10^{-6}\%$	Bismuth	42
	Tartrate-fluoride solution, hydroxylamine HCl	-0.5, cl	MS-Cu: electrolysis, AI: Sn		43
		-0.5, cl	MC: extraction of diethyldithiocarbamate, $S = 10^{-7}\%$	Common salt	5
	Thiourea, HNO_3	op	AI: Cu, Zn, Cd, Bi; Pb content 0.7-1.3%	Alloys, ores	15
	NH_4CNS , urotropine	op	MC: extraction of diethyldithiocarbamate	Ores	44
	HCl	cl	MS: extraction of Pb and Cu diethyldithiocarbamates and reextraction of Pb with N HCl	Copper concentrates	45
	HCl	ap	Silver electrode, $S = 1.6 \times 10^{-6}\%$, conditions of determination investigated	Sodium chloride	11
	HCl	-0.5, op	MC: extraction of PbI_2 with hex-one	Steels	46
Pb	Hydroxylamine chloride		Method for determination of 0.01-2% Pb	Americium dioxide	47
	KOH	sq	Decomposition of sample with HNO_3 + HCl mixture	Arsenic	24
	Triethylenetetraminete-traacetic acid	cl	MS Te: extraction of bromide	Indium concentrates	14
Ti	Salicylate and thiosalicylate	-0.79, cl	Investigation of complex formation and analytical application	Steel Niobium and tantalum oxides	43
	Pyrophosphate, pH 0.5-2.0	-0.19, op	AI: Fe, Cr, Mn, Ni		49
	Sulfuric and oxalic acids	-0.36, pp	S: $10^{-4}\%$, CI: Nb, Ta		22
	Ethanolic HCl solution, $\text{H}_2\text{C}_2\text{O}_4$	cl	Development of method. Error 0.05%	Titanium (III) chloride	50

TABLE 1 (continued)

Element	Supporting electrolyte	Half-wave potential and type of polarography	Characteristics of method	Material analyzed	Source
Zr	H ₂ SO ₄ -H ₂ O ₂	cl	Effect of conditions on catalytic current, $S = 1.5 \cdot 10^{-5}$ g Zr in 20 ml		51
Hf	LiCl in ethanol	-1.5, cl	Investigation of polarographic behavior		52
Th	Solochrome violet, tartrate, pH = 12	-0, 6, -1, 1, cl	By decrease of dye wave. II: Sb, Pb, Co, Ti, V, Zr, Fe, Ni		53
NO ₃ ⁻	Zirconium oxychloride	-0.9, cl	By reduction wave of zirconium nitrate complexes		54
Sb	1-N HCl	-0, 2, ap	AI: Pb, Zn, Cd, In, Sn, Cu, Bi, $S = 2 \cdot 10^{-6}\%$	Tin	55
	0.2-N HCl	-0, 1, ap	MS: volatilization of GeCl ₄ , $S = 2 \cdot 10^{-7}\%$	Germanium, germanium tetrachloride	56
Bi	0.2-N HCl	-0, 005, ap	MS: volatilization of GeCl ₄ , $S = 3 \cdot 10^{-7}\%$	Germanium, germanium tetrachloride	56
	HCl	op	MC: extraction of diethyldithiocarbamate	Ores	44
	Sodium gluconate in alkaline solution	-0, 8, cl	Investigation of complex formation		58
	HCl	-0, 14, pp	MS: Hg cathode	Cobalt	57
V	NH ₄ OH-NH ₄ Cl pH 8-9	-1, 2, pp	Sample evaporated, residue treated with HNO ₃ + HCl	Oil products	59
Nb	H ₂ SO ₄ -H ₂ O ₂	-0, 5, cl	Investigation of conditions and mechanism of reduction, $S = 1.5 \times 10^{-5}$ g/20 ml. II: Mo, W, V, Ta, Zr, Fe		60
Ta	H ₂ C ₂ O ₄ -H ₂ O ₂	cl	Mechanism of catalytic reduction of peroxide, optimum conditions for determination. AI: Mn ²⁺ , Zn ²⁺ , Cr ³⁺ , Pb ²⁺ , Cu ²⁺ , Hg ²⁺ , Al ³⁺ , Ni ²⁺ , Co ²⁺ , Ti ^{IV}		61
O	LiCl in ethanol	-0, 67, op	Development of method	Benzene	62
S	NaOH	-0, 7, ap	Preliminary separation by reaction $Hg + HS^- + OH^- \rightarrow HgS$ and determination of the current $Hg^{2+} \rightarrow Hg$		63
Se	2-N HCl	-0, 01, op	Sample decomposed by HNO ₃ + HCl; error of determination 4%	Semiconductor materials	39
	NH ₄ OH-NH ₄ Cl	pp	MC: reduction by thiosulfate and hydroxylamine, $S = 2 \cdot 10^{-5}\%$	Antimony, indium, gallium, bismuth	64

TABLE 1 (continued)

Element	Supporting electrolyte	Half-wave potential and type of polarography	Characteristics of method	Material analyzed	Source
Te	KCl. pH 1.5-2.5	pp	MC: reduction by thiosulfate and hydroxylamine, $S = 2 \cdot 10^{-5}\%$	Antimony, indium, gallium, bismuth	65
Mo	HF and H_2SO_4	-0.06, -0.52, cl	AI: Ti, Zr, Nb, Ta, W	Niobium alloys	66
	H_2SO_4 and H_2O_2		MC: extraction with dithiol	Plants	67
	H_2SO_4 and KNO_3	-0.2, cl	By catalytic current of nitrate. II: Fe, Cr. AI: W, Cu, $S = 5 \cdot 10^{-6}$	Indium	68
			By catalytic current of nitrate. $S = 0.005$ mg/ml. MS: ion exchange, extraction	Titanium, aluminum, chromium, manganese, tungsten, and others	69
W	H_2SO_4 and H_2O_2 Tartaric acid	-0.4, -0.7 cl	MC: extraction with dithiol Choice of best supporting electrolyte for 0.1-200 mg/ml W	Plants	67 70
U	H_2SO_4	-1.5, ap	Investigation of conditions for polarography, $S = 2 \cdot 10^{-3}$ μ g/ml		71
Mn	Triethanolamine, alkali, sodium sulfite	-0.45, op	Sample decomposed by HNO_3 + HCl mixture	Magnetic materials, ferrites	12
		ap	Method for determination 1 ng Mn. II: Co, Mo, W		72
Fe	Triethanolamine, ethylenediamine, alkali	cl	AI: Pb, Cd, Sn, Mg. II: excess Pb and Cd. Error 4%	Zinc	7
	Triethanolamine, alkali, or ammonium hydroxide	-1.0, -1.4, op	Sample decomposed by HCl + HNO_3 mixture	Magnetic materials	12
Co		cl	Decomposition by HF + H_2SO_4 mixture	Rocks	10
	Pyridine-KCl-mannitol	-1.08, op	Sample decomposed by HCl + HNO_3 mixture	Magnetic materials	12
Ni	NH_4OH , NH_4Cl , KCNS	-1.12, op	MC and MS: precipitation with zinc	Zinc electrolytes	73
	Ditto	-1.12, op	MC and MS: precipitation with zinc. AI: Cu, Cd	Zinc electrolytes	74
	KOH-dimethylglyoxime	-1.16, cl -1.44, cl	Investigation of conditions for reduction of nickel oxide complex with dimethylglyoxime		75
	Pyridine-KCl-mannitol	-0.75, cl	MS: Zn and Cd by ion exchange. Fe masked with mannitol. $S = 1$ ng Ni	Lumino-phors-zinc and cadmium sulfides	76
	HCl-potassium tartrate	-1.15, ac	Simultaneous determination of Ni and Cu in nickel dimethylglyoximate precipitate		6

TABLE 1 (continued)

Element	Supporting electrolyte	Half-wave potential and type of polarography	Characteristics of method	Material analyzed	Source
	Pyridine, triethanolamine, and NH_3 Pyridine-KCNS, pH = 5.5	cl -0, 8, -1, 18, op -0, 6, op	MC: precipitation by hydru- beanic acid for separation from Fe, Al, Cr Sample decomposed with a $\text{HCl} +$ HNO_3 mixture $S = 10^{-5} - 10^{-6}\%$ Ni	Rocks Magnetic materials Cobalt and its salts	10 12 77
Pt		ap	From decrease of sulfur-ion peaks		17
Ce	Acetate buffer solution, pH = 4-5	-0, 9, -1, 0, cl	Anodic concentration of $\text{Ce}(\text{OH})_4$ on graphite electrode and determi- nation of cathodic current	Rare-earth elements	78
Tc	Neutral and alkaline solu- tions	-0, 8, -1, 1, ac, cl	Investigation of nature of waves		79
Pu	Sodium citrate, pH = 4.5	-0, 42, sq	MS: Ion exchange	Uranium alloys, plu- tonium	80
Yb and Eu	Acetate buffer solution	-1, 5,	AI: other rare-earth elements	Monacite sand	81

The development of the method of film polarography, i.e., electrochemical concentration of elements by deposition on the electrode as hydroxides or other insoluble compounds, has continued [105-108]. It was shown that anodic oxidation of manganese (II) and cerium (III) ions at an acidity corresponding to the formation of hydroxides of the cations at higher valency allows the formation of a film of hydroxides on the electrode, by which concentration can be achieved. By determining the cathodic current of electrodisolution it is possible to determine the concentration of the elements in the original solution. The method was also used for the concentration and determination of chlorides, bromides, iodides, sulfides, tungstates, molybdates, vanadates, chromates, organic acid ions, and others. To increase the sensitivity of concentration the solubility of the deposits formed on the electrode would have to be reduced, by adding ethanol for example.

Not only the mercury electrode but also electrodes of other materials, for example graphite, are suitable for this method. A method has been developed for the determination of microquantities of cerium in a mixture of rare-earth elements [78], and also a method for continuous control of heavy-metal content of electrolytes in zinc production and of thallium content in copper, cadmium, and indium compounds. Cathodic films of PbCrO_4 , PbSO_4 , and $\text{Cd}(\text{OH})_2$ have been used to determine lead and cadmium [109].

Catalytic reduction waves for nitrates or hydrogen peroxide have been used for determination of trace quantities of catalyzing elements which do not give good waves [28, 51, 54, 60, 68, 69, 110, 111]. Thus aluminum can be determined from the wave for catalyzed reduction of nitrate ions [28]. Traces of many inorganic and organic compounds catalyze the polarographic reduction of hydrated indium ion [110]. This gave the possibility of determining halides, thiocyanates, and organic compounds containing nitrogen and sulfur. Investigation of the reduction of nitrates and hydrogen peroxide in the presence of zirconium showed that in both cases the catalytic effect arises from the formation of nitrate or peroxy complexes of zirconium [51, 54]. With a method based on this reaction it is possible to determine 10^{-5} g Zr.

Sensitive methods have been proposed for determination of niobium and tantalum [60, 61]. Molybdenum can be determined by the nitrate current at concentrations of 10^{-8} mole/liter [68] or 0.005 mg/ml [69]. It has been found [112] that molybdenum has a catalytic effect on the polarographic reduction of vanadium. A method has been developed for the determination of $10^{-6} - 10^{-16}$ g cyanide [113].

It is proposed that copper can be determined in the presence of large amounts of iron by masking the latter with an alkaline solution of trihydroxyglutaric acid [4]. With a supporting electrolyte containing thiourea a well-defined peak is obtained for silver ions by the oscillographic method [15]. For the determination of commensurate amounts of lead and tin when present together a mixed tartrate-fluoride solution proved suitable and gave separate waves for each element [43]. For tin it was suggested [40] that perchlorate, ammoniacal, or tartrate solutions of 3-mercaptopropionic acid should be used. Here a well-defined wave is obtained over a wide range of acidity. Gallium can be readily determined against an alkaline solution of glycine at pH = 8 [30].

The behavior of titanium complexes of salicylic and thiosalicylic acids has been investigated [48]. For analytical purposes a saturated solution of thiosalicylic acid may be used, where the titanium wave appears at -0.785 V. A mixture of perchloric acid and pyrogallol is a good supporting electrolyte for titanium [114]. For hafnium it is suggested [52] that an ethanol-water solution of lithium chloride is used; a methanol-water solution is used for the determination of zirconium [115].

It is recommended [66] that a mixture of 0.5 M solutions of hydrofluoric and sulfuric acids should be used for the determination of molybdenum in the presence of large amounts of zirconium, niobium, tantalum, titanium, and tungsten, where the molybdenum wave appears at -0.06 V. The behavior of molybdenum in acid chloride solutions has been investigated [116]. Microgram quantities of tungsten can be readily determined by polarography in solutions of mixtures of 10 M perchloric and 0.7 M tartaric acids [70]. With a supporting electrolyte containing triethanolamine and potassium hydroxide [12] separate waves can be obtained for copper, iron, nickel, and zinc.

The use of water-dioxane solutions for determination of cadmium has also been investigated [117]. Complexes of uranium with benzohydroxamic acid [118] and its polarographic behavior on hydrolysis [119], complexes of uranium with pyrophosphate [120], and the effect of additions of surface-active agents on them have been investigated.

Regrettably in the majority of papers cited the choice of supporting electrolytes required is somewhat empirical. Proper attention is not paid to the chemical mechanisms of the complex-forming processes in the solutions or to the establishment of a relationship between these processes and the polarographic characteristics of individual elements.

Indirect Methods of Determination of Elements

The development of methods for polarographic determination of inactive ions by converting them into complex compounds with organic dyes has continued. For thorium a method involving solochrome violet is recommended [53]. In alkaline solution (pH = 12) with sodium tartrate this dye gives a wave at -0.6 V, while the thorium complex appears at -1.1 V. The height of the first wave is inversely proportional and that of the second wave is directly proportional to the thorium concentration. Both waves are suitable for determination of the element. A similar method can be used for the determination of zirconium and hafnium [121]. Germanium forms a complex with alizarin red [38], which gives a polarographic wave with a height proportional to the germanium concentration.

The behavior of complexes of manganese, lanthanum, yttrium, zinc, magnesium, calcium, and aluminum in a solution of solochrome violet at pH = 13 was investigated [122]. The properties of these complexes were used for the determination of trace quantities of magnesium in calcium [123]; the latter does not form a polarographically active complex with solochrome violet; the wave of the magnesium complex appears at -0.88 V.

Methods for Removal of Interfering Ions

In a series of papers, Kovalenko and his coworkers have further developed the combined method of electrochemical analysis, where interfering elements are previously removed by electrolysis. Lead is determined polarographically [43] after removal of copper and tin by electrolysis; nickel is determined in a zinc electrolyte after precipitation with zinc [73-74]. As before the extraction method has not lost its importance. It is recommended [14, 31, 35] that indium should be removed by extraction from chloride or bromide solutions with diethyl ether before polarographic determination of Tl, Cu, Pb, Cd, and Te. In the polarography of gallium its chloride is extracted with a mixture of benzene and butyl acetate [30], by which means it is separated from Cu, Cd, Pb, Sn, Ni, Co, Fe, and Mn. Germanium is separated from indium by extraction of GeCl_4 with carbon tetrachloride [36], after which the determination is completed by polarography.

In the analysis of copper concentrates [27] cadmium is extracted from an aqueous solution of potassium bromide by a solution of diantipyrylmethane in chloroform; it is recommended also [25] that copper be separated from cadmium by extraction with a solution of neocuproin (2,9-dimethyl-1,10-phenanthroline) in chloroform. This

method is used for the determination of cadmium in steels. In steel analysis lead is removed [46] from a solution containing divalent iron by extraction of the iodide with isobutyl methyl ketone. In the analysis of ores lead and bismuth are extracted [44] with a solution of diethyldithiocarbamate in chloroform and then reextracted with 2 M (lead) and 6 M (bismuth) hydrochloric acid. In the analysis of copper concentrates [45] lead and copper are extracted from 1 N hydrochloric acid with a solution of diethylammonium diethyldithiocarbamate in chloroform followed by reextraction of the lead with 4 N hydrochloric acid. By this method lead is also separated from Bi, Sb, Sn, Mo, and As. Extraction of lead and copper diethyldithiocarbamates is also used in the analysis of common salt [5].

Zinc is separated from iron and copper [23] by extraction from a solution of pH 4 containing ammonium thiocyanate with a solution of diantipyrylmethane in chloroform. A method for determination of molybdenum and tungsten in plants is based on the extraction of complexes of these elements with dithiol [67]. Methods are also recommended for the volatilization of germanium [37] and separation of zinc and cadmium by ion exchange before polarography of nickel in luminophors.

Polarography in Molten Salts

The polarographic behavior of nickel in a molten mixture of lithium and sodium fluorides has been investigated [124]. By anodic polarography it is possible to determine trace quantities of this element directly in the melt. Reduction of the nickel to metal occurs at -0.2 V with respect to a platinum electrode.

A rotating disk electrode was used [125] to determine the half-wave potentials for the reduction of rare-earth oxides (La, Gd, Ce, and Eu) in molten sodium bisulfate; their other polarographic characteristics were also investigated. The polarography of bichromate, bismuth, and thallium oxides [126], halides, sulfides, and nitrites [127] in molten carbonates on a gold electrode was investigated, and it was shown that the waves obtained conformed to the Heyrovsky-Ilkovic equation. The reduction of bromides and iodides has been studied [128] in the molten LiNO_3 - NaNO_3 - KNO_3 eutectic with a rotating disk electrode, and the relationships governing the limiting current of these substances were determined.

Other Investigations

The replacement of the mercury dropping electrode in oscillographic polarography by a silver-amalgam electrode has been investigated [129]. The expediency of such a replacement was demonstrated in the case of the oscillographic determination of copper, thallium, cadmium, and zinc. The polarographic waves are of the normal shape, and the limiting currents for the elements mentioned are proportional to their concentrations. For the oscillographic determination of halides a silver electrode has been proposed [130]; the effect of various factors on the characteristics of the polarograms was investigated, and it was shown that the halide ions could be determined separately or simultaneously at concentrations of 10^{-6} mole/liter. Microquantities of cadmium, lead, and manganese were determined [131] by the method of reverse surge currents at concentrations of 10^{-7} mole/liter.

A mercury dropping electrode of teflon is proposed [132, 133] for polarography in aggressive media; the electrode was used to investigate the polarographic characteristics of lead ions, and its practicability for polarography was demonstrated.

It has been shown [134] that alternating current polarography, like the classical method, is suitable for investigation of the composition and stability of complex compounds in accordance with the usual equation relating the half-wave potential shift to the instability constant. The validity of this conclusion was verified for the case of cadmium ammoniate. A method is proposed [135] for calculating the concentrations of two substances with close half-wave potentials on the basis of the additivity of their limiting currents and the various slopes of the calibration curve.

The polarography of dysprosium, ytterbium, and europium has been investigated [136, 81]. The last two were determined in the presence of other rare-earth elements in monacite sand. The behavior of a number of complex compounds in polarography has been investigated: silver cyanide [137], chloride complexes of rhodium [138], thiocyanate complexes of cobalt; it was found that the cobalt was progressively reduced to the monovalent state [139]. Cyanide-ethylenediamine complexes of cobalt [140], chromium complexes [141, 142], and ethylenediamine complexes of nickel [143] have been investigated.

The effect of oxygen on the determination of cadmium by oscillographic polarography [144], the reduction of bichromate ions [145], the reduction of selenium [146] in sulfuric acid solution, and the reduction of tellurium [147] have been investigated.

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