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Extraction Polarography and Its Analytical Applications

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The review is devoted to extraction polarography as a method for the determination of microelements. The possibilities of polarography in combination with a preliminary chemical separation of the elements by extraction are discussed. The types of extraction-polarographic systems known at present are described. It is shown that the selectivity of extraction separations increases if the reagents form complexes with the ions to be determined, which are manifested by effects on the polarisation curves at different potentials. The influence of extracting and ionising solvents on the analytical signal is examined from the standpoint of modern ideas of the chemistry of coordination compounds in non-aqueous media. Examples of the use of extraction polarography for the determination of microelements are presented.
The bibliography includes 116 references.

CONTENTS

I. Introduction 74
II. The role of the organic solvent in extraction polarography 75
III. Types of extraction-polarographic systems 77
IV. The use of extraction polarography in the determination of metals 79

I. INTRODUCTION

The usefulness of the preliminary concentration, by extraction in the form of complexes of the metal ions to be determined, has begun to attract attention recently. The metals are determined directly in the organic extracts[1-4]. The combination of separation and concentration with subsequent determination by physicochemical methods has proved to be one of the most promising fields in chemical analysis. In many instances such combination has become so intimate that it is possible to distinguish a new category of analytical methods which have been called hybrid[3].

Extraction-photometric, extraction-spectroscopic, extraction-polarographic and extraction-radioactive methods as well as extraction chromatography and extraction emission and atomic-absorption flame photometry can be included among the hybrid methods. The simultaneous application of concentration by extraction and of a sensitive apparatus greatly extends the scope of analytical methods. The selectivity of the analysis can be varied both as a function of the type of extraction system (reagent, acidity of the phase, etc.) and as a function of the method of measurement of the analytical signal. The use of a hybrid method in which preliminary extraction determines the absolute and relative concentrations of microelements in combination with an appropriate detection method permits in certain cases the analysis of multicomponent systems. Extraction polarography is one such method.

The present review surveys the results of studies in the field of extraction polarography during the last five years. The first investigations up to 1971 have been summarised in a familiar monograph[1] and also in a review[5]†. Since then the number of publications on extraction polarography has increased continuously. The interest in this method is explained by its universality, simplicity, the rapidity of analysis, the possibility of the simultaneous determination of a group of elements, and the lack of the need for re-extraction with associated inevitable losses.

The polarography is carried out by different methods. The use of versions such as oscillographic and a.c. polarography and catalytic hydrogen currents greatly enhances the scope of the extraction-polarographic methods. In examining the possibilities and advantages of the direct polarography of the extracts, one should note the first studies carried out by amalgam polarography with accumulation[11-15]. In this case concentration of the metal on the stationary electrode was achieved by electrolysing the solution of the test metal (in the form of a complex in an organic solvent). The essential feature of the method of extraction polarography with accumulation consists in the determination of traces of elements directly in the extracts. In this case one carries out a double concentration—by extraction and electrochemically[16-20].

However, the possibilities of the extraction-polarographic methods have been by no means exhausted—one should note in the first place an empirical approach to the selection of both the reagents for the binding of the metal in a complex and of the polarographic conditions as well as the method of recording the polarisation curves itself. The medium in which the polarography is carried out consists of at least two solvents. One of these is used to extract the metal in the form of a complex and the other to ensure the solubility of the supporting electrolyte and the conductivity of the medium. Consequently the second component must have a fairly high dielectric constant. The ratio of these components influences the analytical signal.

The combination of extraction and polarography gives rise to new possibilities and advantages. For example, the employment of non-aqueous solvents for polarography extends the range of potentials in which experiments can be performed as well as the range of values of $E_{1/2}$ for the reduction of ions bound in complexes. Hence it follows that the study of the influence of the nature of the solvent is an essential stage in the development of extraction-polarographic methods.

A conscious choice of rational conditions for extraction-polarographic determinations is impossible without knowing the electrochemical properties of the corresponding complexes. The knowledge of the mechanism of the electrode process permits rational extraction-polarographic determinations with recording of the maximum possible analytical signal. It is then possible to employ specifically polarographic characteristics such as the reversibility of the reduction, the maximum number of electrons involved in a particular stage, the adsorbability and associative accumulation of the substance on the surface of the electrode, and other ways of increasing the sensitivity and selectivity.

†The work of the Kiev School of Analytical Chemistry[6-10] has made a definite contribution to the development of the extraction-polarographic methods.

Only after such studies is a foundation laid for the selection of the optimum polarographic conditions ensuring a fairly low concentration limit in the determination and a high selectivity of extraction-polarographic analyses.

II. THE ROLE OF THE ORGANIC SOLVENT IN EXTRACTION POLAROGRAPHY

The solution for polarography must have a fairly high conductivity. However, extracts are not as a rule electrolytes. It is therefore necessary to add to the extract solvents with a high dielectric constant containing a specific amount of supporting salts, ensuring a high conductivity. Thus homogeneous mixtures of extracting and ionising solvents are used in extraction polarography. The ratio of the mixture components is determined by the solubility of the extracted complex and of the supoorting salt. In terms of their electrical conductivity, such systems are not inferior to the traditional polarographic electrolytes[1].

The nature of both the extracting and ionising organic solvents can influence the stability of the complexes formed in the "metal ion–organic reagent" system. However, in most cases the depolariser is the metal chelate with a fairly high stability. The complex formation equilibrium and hence the question of the predominance of a particular complex species in the polarographed extract are not of decisive importance. This is particularly valid in relation to a large group of the so-called inert complexes. In order to solve problems associated with the increase of the selectivity and sensitivity of the analysis, it is necessary to make a rational choice of the extracting solvent, since it influences the parameters of the polarographic waves and hence the analytical signal. The most important factor for the analytical chemist is information about the properties of the limiting current recorded on the voltamperograms as a function of the nature of the organic solvent.

Table 1. The properties of extracting and ionising solvents at 20 °C.

Solvent	ε	η, cP	DN(SbCl$_5$)[28]	Solvent	ε	η, cP	DN(SbCl$_5$)[28]
Extracting solvents				Extracting solvents			
Benzene	2.28	0.70	4.9	Ethyl acetate	6.40	0.47	17.1
Toluene	2.38	0.63	—	Butyl acetate	5.01	0.73	—
m-Xylene	2.36	0.62	—	Pentyl acetate	4.75	0.92	—
Chloroform	4.80	0.59	—	Isopentyl alcohol	15.64	4.8	—
Carbon tetrachloride	2.24	—	—	Ethyl methyl ketone	18.51	0.42	—
				Butyl alcohol	17.0	3.37	29.0
Ionising solvents				Ionising solvents			
Acetonitrile	38.80	0.34	14.1	Methyl alcohol	33.60	0.54	19.0
Acetone	21.24	0.30	17.0	Ethyl alcohol	25.80	1.09	—
Dimethylformamide	37.65	0.79	26.6	Formamide	111.50	3.76	39.1
Dimethyl sulphoxide	48.90	1.96	29.8				

The physical constants of the most important solvents of both types are listed in Table 1. The influence of the nature of the extracting solvent on the height of the polarographic waves (i_{lim}) has been studied in relation to hydroxyquinolinates[7], benzoylphenylhydroxylaminates (BPHA),[9] *N*-cinnamoylphenylhydroxylaminates (CAPHA),[21] 4-benzoyl-3-methyl-1-phenyl-5-pyrazolonates[22], dithiocarbamates (DTC),[23–27] ethylxanthates (EXT),[25,26] dithiophosphates (DTP),[26,27,29] 8-mercaptoquinolinates[30,31], and tri-n-octylaminates (TOA).[32]

Useful information about the influence of the solvent on the reduction process can be obtained by comparing the polarographic characteristics of the complexes in aqueous (whenever possible) and non-aqueous media. The height of the reduction wave of copper(II) ions in the presence of 8-hydroxyquinoline in a non-aqueous solution (a mixture of toluene and methanol) is almost twice as high as in an aqueous solution[6]. The change in the limiting current in non-aqueous solvents compared with water is attributed to the change in the viscosity of the solution, which influences the diffusion coefficient of the depolariser[6]. However, such a difference between the values of i_{lim} is not always a consequence of the influence of the viscosity of the medium alone. Whereas in an aqueous solution copper(II) is reduced in the form of the aquo-ion, in the toluene–methanol system being compared it is reduced as the 8-hydroxyquinoline complex. One cannot agree with the postulate[6] that the complex dissociates prior to the electrode process: like other chelate complexes, the 8-hydroxyquinolinates usually do not dissociate in organic solvents[34]. It is therefore also impossible to account for the difference between the diffusion current constants by the non-identical electrochemical behaviour of the depolariser in aqueous and non-aqueous media, which should be reflected, like the viscosity of the solution, in the diffusion coefficient. For this reason, the use of non-aqueous media can apparently entail in many instances a decrease of i_{lim} compared with an aqueous medium[12,13].

In order to elucidate the influence of the nature of the organic solvent, it is more useful to investigate the same complex in different extracting solvents. The viscosities of the pure extracting solvents can be used to establish the relation between the viscosity of the solution and the limiting current for the reduction of the complex. The ionising solvent must be the same under these conditions and the ratio of the extracting and ionising solvents must be constant. Such a study has been made by Pyatnitskii and Ruzhanskaya in relation to copper, lead, and iron hydroxyquinolinates[7] and copper, iron, and indium benzoylphenylhydroxylaminates[9]. The results showed that the nature and properties of the solvent (Table 1) have a considerable influence on the height of the polarographic waves and hence also on the lower limit of the determination. In the general case the wave height diminishes with increasing viscosity of the solvent, which is due to the familiar inverse proportionality between the diffusion coefficient and the viscosity of the medium (η). On the other hand, the viscosity factor is not always decisive, because the product $i_{lim}\eta^{1/2}$ is not constant in many instances. A similar phenomenon has been observed, for example, in the reduction of metal complexes of CAPHA in mixed organic solvents[21]. Data concerning the influence of the nature of the extracting solvent on i_{lim} for the waves due to the metal complexes of dithiocarbamic, dithiophosphoric, and xanthic acid derivatives[23–27] show that the change in i_{lim} is related not only to the viscosity of the solvent but also to its capacity to solvate the depolariser species. The change in the degree of solvation of the complexes leads to the formation of solvates whose diffusion coefficients differ greatly and this is also reflected in the values of i_{lim}. The decrease of the limiting current for the reduction of iron(III) and zinc(II) dimethyldithiocarbamates in the sequence ethyl acetate > butyl acetate > pentyl acetate is probably associated with the fact that the complex solvated by ethyl acetate molecules is smaller than in pentyl acetate[23]. The increase of the size of the solvate in the above sequence entails a decrease of the diffusion coefficient of the complex. The highest limiting

current in the determination of metals as their complexes with organic ligands can be attained in the polarography of benzene extracts.

On passing to chelates of metals whose ions are more highly solvated (copper and cadmium), the change in i_{lim} with the change in the nature of the solvent is more distinct. For example, cadmium complexes of DTC in solutions in aromatic hydrocarbons in the presence of 0.2 M lithium perchlorate in methanol as the supporting electrolyte are reduced reversibly, whereas in acetate esters and in dimethylformamide (DMF) the reduction is irreversible[24] (Fig. 1). The tendency towards an increase of i_{lim} on passing from DMF to aromatic hydrocarbons is observed also for other dithiocarbamate complexes, but in the case of cadmium chelates the difference between the currents i_{lim} is particularly notable. This behaviour is associated with the strong solvating capacity of DMF.

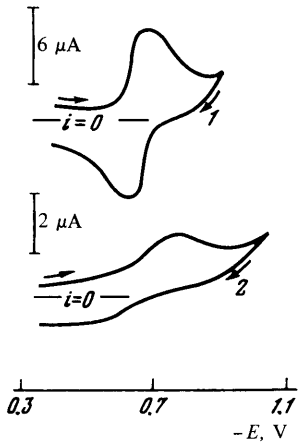


Figure 1. Oscillopolarograms of a 5×10^{-4} M solution of cadmium dibutyldithiocarbamate in an ethanol–benzene mixture (curve *1*) and dimethylforamide (curve *2*); supporting electrolyte—0.2 M lithium perchlorate[24].

Another parameter of the voltamperogram to which attention should be paid in selecting the solvent, the type of reagent for chelating the metal, and other analytical conditions is the velocity constant for charge transfer k_S, which determines the reversibility of the electrochemical system[35]. When $k_S > 10^{-2}$ cm s^{-1}, the electrochemical equilibrium at the electrode is fairly mobile during the recording of the voltamperogram. If there are no intermediate chemical stages, deactivating the electron addition product, then under these conditions the discharge is reversible. By selecting the appropriate organic solvent, it is possible to increase the stability of the electron transfer products and to ensure suitable conditions for the recording of curves with the aid of a.c. polarography. It is impossible to extend greatly the number of reversible electrochemical reactions at the electrode compared with an aqueous medium.

The different degrees of reversibility of the waves due to the complexes are caused by the nature not only of the central atom but also the ligand. Thus in the reduction of iron(III) dithiocarbamates[23] and xanthates[28] in aromatic hydrocarbons the wave corresponding to the transfer of the first electron to the complex species is reversible only in the former instance. The polarographic waves of metal xanthates obtained under the same conditions are as a rule less reversible than those for the dithiocarbamates. The differences in the reversibility of the reduction waves of metal dithiocarbamates and xanthates can be explained by the more marked ability of the xanthates to form comparatively stable solvates for which a slow charge transfer in the electrochemical stage proper is observed. The reduction of the copper(II) complex of CAPHA in oxygen-free extracting solvents is also reversible; in isopentyl and hexyl alcohols the process is irreversible[21]. The irreversible reduction of the complex in carbon tetrachloride is an exception. It has been noted that, on passing to ethyl acetate, the reduction takes place with consumption of one electron. The slow electron transfer has been explained[21] by the adsorption of organic solvent molecules on the surface of the electrode.

The choice of a suitable ionising solvent to increase the sensitivity of the metal also merits attention. Various ionising solvents have been compared[7] (for the same extracting solvent) in relation to 8-hydroxyquinolinates: methanol, DMF, dimethyl sulphoxide (DMSO), and formamide; they differ from one another by their dielectric constants (ε) and viscosities. Analogous studies were made later for metal xanthates[28]. The replacement of methanol by another ionising solvent with a greater solvating capacity leads to a decrease in the height of the wave. On passing to solvents with a greater solvating capacity (DMF, DMSO), the change in i_{lim} becomes more appreciable. The fact that in solvents with similar viscosities the limiting current for the reduction of metal chelates is greater for the solvent with a lower donor number is striking[24]. Furthermore, when ethanol, the viscosity of which is greater than that of DMF (Table 1), is used as the ionising solvent, the i_{lim} observed for the xanthates is approximately twice as great as the current obtained in DMF.

Attempts have been made to explain from different standpoints the influence of the solvent on the parameters of the electrode process[36]. The replacement of one solvent by another can entail an appreciable change in the energy of the activated state, while the energy of the initial state of the chelate remains almost the same. This situation leads to an increase in activation energy for the reaction, i.e. to a decrease of the rate of charge transfer (a decrease of k_S).

On solvation, solvent molecules can enter the inner coordination sphere (particularly for a coordination-unsaturated complex) or remain bound to the complex, occupying a second coordination sphere[36]. In the former case the reduction of the complex is apparently less reversible than in the latter.

In studies of the influence of the organic solvent, both extracting and ionising, on the ease of reduction of complexes attempts have frequently been made to establish a correlation between $E_{1/2}$ and the dielectric constants[7,9,23]. The results of the study of hydroxyquinolinates[6], benzoylphenylhydroxylaminates[9], and dithiocarbamates[23] have shown that, when the solvent is changed, the values of ε are altered somewhat, but a consistent relation between them and the dielectric constants ε (Table 1) is not observed. Nor is there an appreciable change in the differences between the reduction potentials of the metal ions and their sequence. One should note that the displacement of the half-wave potential $E_{1/2}$ along the potential axis when the solvent is altered can be associated with the change in the interphase potential. In estimating the half-wave potential shift under the influence of the solvent, one must also take into account the adsorption of the depolariser[37].

It is of interest to examine the influence of the ratio of the volumes of the extracting and ionising solvents on the characteristics of the polarographic waves. The change in the

volume of the extracting solvent with a low viscosity and a slight solvating capacity (toluene, *m*-xylene, benzene) has almost no influence on the height of the polarographic waves of metal 8-hydroxyquinolinates[7,9], while the increase of the fraction of the extracting solvent with a greater viscosity and a satisfactory solvating capacity (butyl and isopentyl alcohols and cyclohexanone) leads to a decrease of i_{lim}. In order to ensure a better conductivity of the solution, it is sometimes necessary to increase the fraction of the ionising solvent, as happened in the reduction of the indium(III) complex of TOA,[32] the copper(II) complex of dithizon[38], and the molybdenum(VI) complex of BPHA.[39] The influence of η and ε of the extracting solvent is hardly manifested in this instance. The application of the method of differential oscillographic polarography makes it possible to do without ionising solvents altogether. In this method there is no need for a high conductivity of the solution. The low solubility of the supporting electrolyte in the extracts used in the study[40] (butyl and isobutyl alcohols, ethyl methyl ketone, and butyl methyl ketone) nevertheless proved sufficient to permit measurements.

From a practical point of view, solvents with high viscosities and high donor numbers are less convenient, since a rigorous control of the ratio of their volumes is then essential.

III. TYPES OF EXTRACTION-POLAROGRAPHIC SYSTEMS

An effective combination of extraction and voltamperometric methods necessitates a comprehensive knowledge of the characteristics of the electrochemical reactions of metal chelates in the extracting solvents or their mixtures. The general principles by which one must be guided in choosing the polarographic conditions for the solution of chemical-analytical problems can be easily examined in relation to the reduction of a large number of metal complexes with reagents containing different donor atoms in functional-analytical groups.

It is preferable to extract elements in the form of inner complexes and chelates, for which electrochemical processes are less complicated by the preceding and subsequent chemical reactions which influence both on the shape of the waves and their position along the potential axis. Furthermore, chelates are uncharged, which reduces the degree of their solvation and creates suitable conditions for increasing the analytical signal. This is why there is no slackening of interest at the present time in the traditional chelating extractants.

Among the metal chelates extracted by organic solvents, derivatives of dithio-acids and 8-hydroxyquinoline are used most frequently, in practice, as already mentioned. This is associated not only with the ready availability of the reagents but also with the fact that a very wide range of metals generate a current proportional to the metal concentrations in their presence during both electrochemical reduction and oxidation. The conditions for the electrode reactions can then be modified by varying the ratio of the extracting and ionising solvents and by slecting the supporting electrolyte, which makes it possible to apply different versions of polarography for the recording of the analytical signal.

The possibility of the polarography of certain metal dialkyldithiocarbamates in the chloroform–methylcellosolve–water ternary mixture was noted above. Methylcellosolve functions in this instance as a homogeniser for the system, chloroform is the extractant, and water creates conditions suitable for conductimetric measurements[41–43]. However, the use of this system is limited by the comparatively narrow region corresponding to the polarisation of the mercury dropping electrode (m.d.e.)—below −0.8 V relative to the saturated calomel electrode (sat.c.e.). The use of dioxan, dichloroethane, and formamide, in which there is a wide range of cathodic polarisations, in polarographic analysis of chelates involves certain difficulties. In electrochemical reduction in these solvents and their mixtures one frequently records rather indefinite voltage–current curves, which are unsuitable for analysis[7,9]. For many 8-hydroxyquinoline[7] and benzoylphenylhydroxylamine[9] complexes, it has been impossible to observe reduction waves under these conditions.

This is the reason why a search has been made for a solvent system which should not be inferior to chloroform in its capacity to dissolve chelates but would ensure the recording of readily reproducible voltage–current curves, suitable for the measurement of the potential and the current. Such a system is apparently provided by a mixture of aromatic hydrocarbons or acetate esters with methanol, which is added to dissolve the electrolyte salt (ionising solvent). Solvents of the benzene and acetate ester series dissolve readily the majority of complexes with organic ligands, are infinitely miscible with ionising solvents[1,7,13], and are polarographically inactive over a wide range of potentials[7–9]. Furthermore benzene and its analogues have a low solvating capacity (see above), which increases the reversibility of the process and makes it possible to increase the sensitivity of the determination by employing a more effective apparatus. The shape of the voltage–current curves depends significantly also on the concentration of the depolariser, in consequence of its adsorption activity. It has been established for metal complexes of dithiocarbamic acid derivatives that the adsorption phenomena observed in the polarography of such systems are determined by the solubility of the chelates in the given solvent and the position of the polarisation curve relative to the potential axis. The electrochemical reduction of complexes of a large group of metals (Tl, Pb, Cu, Hg, Cd, and Bi) takes place at the m.d.e. near the electrocapillary zero, where complex species with organic ligands are adsorbed to the greatest extent.

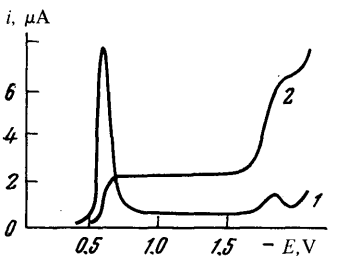


Figure 2. A.c. (curve *1*) and classical (curve *2*) polarograms of a 5×10^{-4} M solution of iron dimethyldithiocarbamate in a benzene–ethanol mixture; supporting electrolyte—0.2 M lithium perchlorate[23].

Thus, in selecting the extraction-polarographic system preference should be given to chelating agents and solvents which would make the electrochemical process reversible to the maximum extent. The presence of at least one reversible stage in the electrode reaction makes it possible to use a.c. polarography for the recording of the analytical signal[23].

The set of the data available at present permits a well-founded approach to the selection of not only the solvent but also of the extraction reagents. The choice of the ligand depends on the problem formulated and the objects of the analysis. If there is a need for an increased sensitivity of the analysis one can recommend dithiocarbamates as extraction reagents, because their complexes are reduced irreversibly in most instances, which makes it possible to employ a.c. polarography for the recording of voltage–current curves[23]. The analytical signals recorded with the aid of classical and a.c. polarography are compared in Fig.2. For extraction from hydrochloric acid solutions, dithiophosphates, which are stable under the given conditions in contrast to dithiocarbamates, are of greatest interest. This is especially important for the determination of elements such as bismuth, antimony, and arsenic, which are almost completely bound in complexes with dithiophosphates only when the acidity of the solution is high[29]. The extraction and hence the polarographic process can be made selective under these conditions by choosing an appropriate pH. Fig.3 presents the dependence of the extractability of metal dithiophosphates on pH in extraction with toluene.

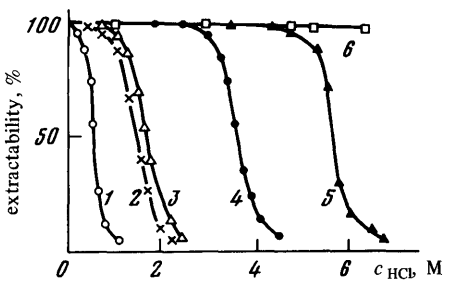


Figure 3. Dependence of the extractability of metal diethyl dithiophosphates on the acidity of the medium: 1) cadmium; 2) cobalt; 3) nickel; 4) lead; 5) bismuth; 6) arsenic[29].

When the complexes are extracted jointly, the polarographic method permits a separate determination of the elements in the same solution. For example, in the extraction of cobalt(II), nickel(II), and zinc(II) dithiophosphate complexes it is impossible to select a pH range where they would be separated, but the polarograms of the solutions in benzene (toluene)–ethanol mixtures shows distinct waves of the metal complexes at different potentials[29] (Fig.4).

Another way of increasing the selectivity in the determination of metals involves the use of metal complexes as extractants. There are very few examples of this type of application of complexes and these refer mainly to dithiocarbamates. The stability of metal complexes of DTA decreases in the sequence Hg(II) > Pd(II) > Ag(I) > Cu(II) > Tl(III) > Ni(II) > Bi(III) > Pb(II) > Co(III) > Cd(II) > Zn(II) > Tl(I) > Sb(III) > Fe(III) > Te(IV) > Mn(II).[44,45] With the aid of this stability series, it is possible to select a complex capable of participating in the extraction exchange with the metal to be determined[46]. Such an extractant complex can consist of a metal complex less stable than the complex of the element to be determined. A necessary condition governing the choice of the extractant is also its ability to be reduced or oxidised in a potential range different from the corresponding range for the dithiocarbamate of the element to be determined. In the determination of palladium(II) this requirement is met by copper(II) dithiocarbamate[47], which is reduced in a 2 : 3 toluene–ethanol mixture at a potential of −0.3 V relative to liquid mercury at the bottom of the cell. When a toluene solution of copper(II) diethyldithiocarbamate is added to an aqueous solution containing palladium(II) ions as well as ions of other elements, palladium(II) is almost completely extracted; other elements are not extracted, which is established on the basis of the absence of the waves of their dithiocarbamates from the polarograms. The copper(II) diethyldithiocarbamate complex has been used as the extractant in the determination of palladium(II) in a combined metallation electrolyte[47].

Zinc(II) diethyldithiocarbamate has been used as an extractant to determine microamounts of copper[48]. Down to 8.5 μg kg^{-1} of mobile copper in the soil can be determined from anodic voltamperograms obtained at a rotating graphite disc electrode in a 2 : 3 toluene–acetone mixture[48]. In procedures based on extraction-exchange reactions the determination is not always carried out directly in the organic extracts. Thus the extraction exchange between the bismuth(III) diethyldithiocarbamate complex in carbon tetrachloride and mercury(II) in an aqueous bromide solution is completed by the equivalent transfer of bismuth(III) to the aqueous phase. Its subsequent determination by inversion voltamperometry ensures a lower limit of detection down to 0.003 μg ml^{-1}.[49]

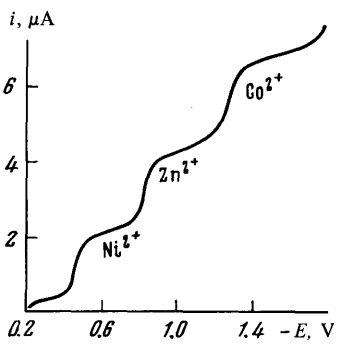


Figure 4. Polarograms of a benzene extract containing 10^{-3} M nickel(II), zinc(II), and cobalt(II) in 0.2 M lithium perchlorate in ethanol as the supporting electrolyte; extractant—diethyl dithiophosphate[44].

An essential requirement which must be made by the extraction-polarographic system is the purity of all its components. Apparently one must not accept without question the stated grade of commercial reagents. Studies have shown[23,24,31] that they require careful purification by repeated recrystallisation from alcohols, acetone, etc. Studies where the choice of rational conditions for the extraction-polarographic determinations based on specially synthesised, purified, and identified complexes, in the form of which the elements are extracted merit attention[50–52]. As regards the purification of solvents, the latter are subjected to fractional distillation in almost all cases. However, since the solvents are added to aqueous solutions in the extraction process, it is not always essential to dry them carefully. This is necessary only in those cases where the solvent hydrolyses when stored in the presence of an admixture of water with formation of polarographically active compounds. Table 2 presents the most typical extraction-polarographic systems used for the analysis of various elements.

Table 2. Types of extraction-polarographic systems.

Reagent	Solvent mixture	Method of recording	Polarisation potential of electrode	Elements determined	References
1. Sodium diethyl dithiocarbamate	chloroform – methylcellosolve – 0.1 M $HClO_4$ ($KClO_4$)	I, II	0.0 – –0.8 V	Bi(III), Cu(I), Cu(II), Tl(I), Pb(II), Hg(II)	41–43,50,51
2. Dithiocarbamates ($R_2NCS_2^-$, R = CH_3, C_2H_5, or n-C_4H_9) (n = 4, 5)	benzene, toluene, *m*-xylene, ethyl acetate, butyl acetate, pentyl acetate—0.2 M $LiClO_4$ ($NaClO_4$) in methanol or ethanol	I–III	+0.2 – –1.8 V**	Pb(II), Cd(II), Sn(II), Cu(II), Bi(III), Tl(I), Fe(III), Zn(II), Mn(II)	23,24,52,55
	benzene, toluene, chloroform, carbon tetrachloride—0.2 M $LiClO_4$ in acetone	IV	0.0 – +1.9 V**	Cu(II), Ni(II), Zn(II), Tl(I), Pb(II)	48,58,59
3. Alkyl xanthates ($ROCS_2^-$, R = CH_3, C_2H_5, n-C_3H_7, or iso-C_3H_7)	benzene, toluene, *m*-xylene, ethyl acetate, butyl acetate, pentyl acetate, pentyl and isopentyl alcohols, heptane—0.2 M $NaClO_4$ in ethanol	I, III	+0.3 – –2.0 V***	Fe(II), Fe(III), Ni(II), Zn(II), Cd(II), Pb(II), Sn(II), Tl(I), Bi(III), Sb(III), As(III)	25–28
($ROCS_2^-$, R = n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, or iso-C_5H_{11})	toluene (chloroform)—0.2 M $LiClO_4$ in acetone	V	0.0 – +1.9 V**	Ni(II)	59
4. Diethyl hydrogen dithiophosphate	toluene (benzene)—0.2 M $LiClO_4$ in ethanol	I, III	+0.1 – –2.0 V***	V(IV), Cr(III), Mn(II), Co(II), Fe(II), Fe(III), Ni(II), Zn(II), Cd(II), Pb(II), Bi(III), As(III), Sb(III), Tl(I)	26,27,29
5. 8-Mercaptoquinoline	benzene, toluene, *m*-xylene, pentyl acetate, isopentyl alcohol—0.1 M LiCl in ethanol	I	–0.2 – –2.0 V***	Hg(II), Cu(II), Cr(III), Mo(VI), Zn(II)	30
6. 8-Hydroxyquinoline	benzene, toluene, *m*-xylene, pentyl acetate, butyl acetate, chloroform, dichloroethane, pentyl and butyl alcohols, cyclohexanone—0.1 M LiCl in methanol	I	–0.2 – –1.2 V	Cu(II), Pb(II), Fe(III), Cd(II), Bi(III)	7
	fused naphthalene-DMF —0.1 M $HClO_4$ + 0.1 M NaClO	I	0.0 – –1.0 V	Mo(VI), Cd(II), Pb(II), In(III)	61,62
	isobutyl methyl ketone, supporting electrolyte—0.1 M $(C_4H_9)_4NClO_4$	I	0.0 – –1.3 V	Cu(II)	63
7. *N*-Benzoylphenyl-hydroxylamine	benzene, *m*-xylene, butyl, pentyl, and isopentyl alcohols—0.1 M $(C_4H_9)_4NClO_4$ in methanol, DMF, formamide, and DMSO	I	-0.2 – -1.6 V (pH of aqueous phase 5 - 10); -0.2 – -0.9 V (pH of aqueous phase 3)	Pb(II), Cu(II), Cd(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Zn(II), Pd(II), Bi(III), Ti(IV)	70,71
8. *N*-Cinnamoylphenyl-hydroxylamine	pentyl alcohol, ethyl acetate, benzene—0.1 M LiCl in methanol	I	0.0 – –1.2 V	Cu(II), Cd(II), Pb(II), Ga(III), In(III), Tl(III), Fe(III), Bi(III), Ti(IV), V(V), W(VI), Mo(VI)	72–75
9. Salicylaldoxime	toluene—0.1 M LiCl in methanol	I	–0.2 – –1.5 V	Cu(II), Pd(II), Pb(II), Cd(II), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Zn(II), Bi(III), Ti(IV)	8
10. Phenoyltrifluoro-acetone	benzene—0.1 M LiCl in methanol and butanol—acetophenone mixt.	I	-0.2 – -0.75 V (pH 4.1); -0.2 – -0.6 V (5 *N* HCl)	Cu(II), Tl(I), Pb(II)	8
	isobutyl methyl ketone—0.1 M acetylacetone - acetate buffer at pH 5.8	I	0.0 – –1.5 V	Fe(III)	100
11. 4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone	cyclohexanone, dichloroethane, ethyl acetate, chloroform, toluene, benzene—0.75 M NH_4Br in ethanol	I	0.0 – –1.2 V	In(III)	22
12. Dimethyl-α-furyl-, and α-benzyl-glyoximes	toluene, 1 M ammonia buffer in ethanol	I–III	–0.2 – –1.8 V*	Ni(II)	85
13. Acetylacetone, phenoyl-trifluoroacetone	isobutyl methyl ketone, supporting electrolyte—0.1 M $(C_4H_9)_4NClO_4$	I	—	Fe(III)	95,96
14. Diantipyrinylmethane	chloroform—1 M LiCl in ethanol	III	0.0 – –1.0 V	Sb(III), V(V), As(III)	92,93,96
15. Catechol	dichloroethane - diphenylguanidinium acetate	I	0.0 – –1.2 V		116

*Recording methods: I) classical polarography; II) a.c.polarography; III) oscillographic polarography; IV) anodic voltamperometry with a rotating graphite disc electrode; V) ditto with a stationary graphite electrode.

**Potential relative to mercury at bottom of cell.

***Potential relative to removable mercury electrode; in remaining cases relative to a saturated calomel electrode.

IV. THE USE OF EXTRACTION POLAROGRAPHY IN THE DETERMINATION OF METALS

The method of extraction polarography has come to be used comparatively widely in recent years. There has been an increase of the range of reagents investigated and studies have been made on extraction polarography using solid reagents. Among the metal chelates extracted by organic solvents at the present time, dithiocarbamates[18,23–27,47–60], hydroxyquinolinates[6–8,10,15,17,61–69], and substituted hydroxylaminates[9,70–82] have been most fully investigated. There have been reports also of the other reagents; oximes[8,83–85],

xanthates[25-28,56-60,86-91], dithiophosphates[25-27,29,56,60], pyrazolone derivatives[22,92-94], etc.[95-103].

8-Hydroxyquinoline is widely used for concentration by extraction in combination with different versions of polarography. Pyatnitskii and Ruzhanskaya investigated the influence of the nature and properties of organic solvents (benzene, toluene, *m*-xylene, pentyl acetate, chloroform, dichloroethane, pentyl, isopentyl, and butyl alcohols, and cyclohexanone) on the polarographic characteristics of the reduction waves for certain metal hydroxyquinolinates[6,7,10]. On the basis of the results, methods have been devised for the determination of copper in ferrotitanium, titanium-based alloys, alloyed steels, and babbitts[6,10]. Apart from 8-hydroxyquinoline, its various derivatives have been used. Cadmium, cobalt, and iron have been extracted quantitatively with butyl alcohol in the form of their complexes with 8-hydroxyquinoline-5-sulphonic acid with subsequent determination of the metals in the extract down to a lower limit of 7.5×10^{-8} g-ion litre^{-1}.[68]

Studies have been made on the extraction of metal hydroxyquinolinates by extraction amalgam polarography with accumulation using solvents of the benzene series[15,17]. The sensitivity of the determination of the elements by this method is in most cases not less than the sensitivity of the amalgam-polarographic analysis of impurities in aqueous media. The method of extraction polarography with accumulation is promising for the study of the extraction of substances present at low concentrations. The scope of this method has been investigated in the extraction of chelates in relation to the distribution of copper and cadmium *O*-hydroxyquinolinates in systems comprising water and solvents of the benzene series[15,17] and also copper diethyldithiocarbamate in the water–chloroform system[18]. The kinetics of the extraction of complexes with organic solvents and the influence of the pH of the aqueous phase on the extraction have been investigated, the extraction constants for the complexes have been calculated, and the composition of the complexes has been determined. It has been shown that the metal can be concentrated at the electrode either as a result of its transfer to the amalgam in the electrolysis of the solution of the chelate in the extracting mixture (chelate complexes of bismuth, cadmium, lead, thallium, copper, indium, and certain other metals[19]) or as a result of the formation of a colloid metal–mercury system (iron, nickel, manganese, cobalt, etc. compounds).

Extraction polarography with accumulation has been used to determine antimony in solutions of sodium chloride and specially pure hydrochloric acid[54] with the aid of chloroform and sodium diethyldithiocarbamate in the presence of EDTA and potassium iodide. The lower limit of the detection is 5×10^{-6}%. The use of 8-hydroxyquinoline in polarographic analysis has been described by Fujinaga and Puri[65]. Zinc, cadmium, manganese, and magnesium have been determined by an indirect method based on the decrease on the height of the reduction wave for 8-hydroxyquinoline itself in the presence of these metals.

The possibility of employing solid but readily fusible organic substances for extraction had been reported previously[104-106]. Such extraction is carried out in slightly heated solutions where the extractant is fused. After extraction and cooling, the extract solidifies rapidly and the aqueous layer is separated by simple decantation. Extraction by readily fusible substances does not require a separating funnel. A set of readily fusible extractants, permitting the extraction of elements from solutions with different acidities, has been published[106]; these are mainly paraffins in mixtures with various oxygen-containing solvents or with *N*,*N*-dimethyl- and *o*-chloro-aniline. Lobanov et al.[107] studied the possibility of the group concentration of metal ions by an 8-hydroxyquinoline melt. However, extractants of this class are still hardly used.

Several communications have been published recently[61,62,64,65] on the isolation of metal hydroxyquinolinates by extraction into fused naphthalene with subsequent polarography of the dimethylformamide solution of the extract. The use of such extraction-polarographic systems has definite advantages: simplicity of operation, faster attainment of equilibrium as a result of heating, the absence of risk of emulsification, and the disappearance of the need to dilute the solution with an ionising solvent when, for example, dimethylformamide is used, etc. The conditions for the extraction-polarographic determinations of Be, Bi, Mo, Cd, Hg, Ni, Pb, Pd, Sn, Ti, U, V, W, Ce, Cu, Tl, In, Mn, Sr,[65] Mo,[61] Pb and Cd,[63] and In [64] have been investigated. Waves suitable for analytical purposes have been obtained only for Mo, Pb, In, Bi, U, Cu, Pd, and Fe.[65] Other metals investigated do not give rise to reduction waves in the accessible range of potentials, since at potentials more negative than −1.1 V the organic reagent is reduced under these experimental conditions. Evidently it would be useful to find a supporting electrolyte other than pyridine + $HClO_4$ and $NaClO_4$ + $HClO_4$ mixtures, as a result of which the range of potentials for polarography would be narrowed down still further. The number of ions determined in the presence of the above supporting electrolytes is very small. Polarographic activity is not shown by 8-hydroxyquinoline alone. Substituted hydroxylamines and the oximes of certain aldehydes and ketones, which are reduced at an m.d.e., have been used in extraction-polarographic analysis. For example, *N*-benzoylphenylhydroxylamine (BPHA) permits studies in the range from −0.2 to −1.6 V. An increase of the acidity of the aqueous phase narrows down the range in the cathodic region to −0.9 V (pH 3), which can apparently be accounted for by the facilitation of the reduction of the protonated form of the reagent. The polarographic study of the reduction of the complexes was begun by Hudbard and Gernon[70], and thenumber of polarographically active complexes under the conditions employed by them is small: those of Sb, Bi, Cu, In, Fe, Pb, and V. Copper ($E_{1/2} = -0.28$ V relative to the sat.c.e.), iron ($E_{1/2} = -0.56$ V), and lead ($E_{1/2} = -0.62$ V) waves and to a lesser extent antimony ($E_{1/2} = -0.27$ V) and vanadium ($E_{1/2} = -0.62$ V) waves (because their heights are small), are suitable for analytical purposes[70]. Pyatnitskii and Ruzhanskaya[9] investigated the polarographic behaviour of lead(II), copper(II), cadmium(II), nickel(II), zinc(II), iron(III), gallium(III), indium(III), thallium(I), bismuth(III), cobalt(II), titanium(IV), vanadium(V), molybdenum(VI), tungsten(VI), manganese(II), chromium(III), and palladium(II) benzoylphenylhydrozylaminates in isopentyl alcohol and *m*-xylene. The influence of the solvent has been studied for copper(II), iron(III), and indium(III) complexes. It follows from the results that, with decrease of the dielectric constant, the reduction potentials are in most cases displaced to the negative region, but there is no clear-cut regular variation in this instance. The greatest sensitivity of the determinations has been obtained in extraction by weak polar solvents of the benzene series. They also have the advantage that waves with a more definite shape are obtained.

The results of a study of the same metal benzoylphenylhydroxylaminates have been published by Pilipenko et al.[71]; in this case the influence of the solvents was investigated (in contrast to Pyatnitskii and Ruzhanskaya[9]) also for all the remaining benzoylhydroxylaminates. The BPHA complexes of many metals are reduced in benzene, toluene,

dichloroethane, carbon tetrachloride, butyl, pentyl, isopentyl, and hexyl alcohol, ethyl acetate, and ethyl methyl ketone extracts in the presence of 0.1 M LiCl supporting electrolyte and methanol. It was established that the values of $E_{1/2}$ for metal *N*-benzoylphenylhydroxylaminates in organic solvents are displaced towards more negative potentials compared with the $E_{1/2}$ of the metal ions in aqueous solutions as a result of complex formation or solvation. The cathodic shift of the waves in ethyl acetate and pentyl alcohol relative to benzene and chloroform has been explained[72] by the solvating capacity of oxygen-containing organic solvents. In terms of their reduction potentials at the m.d.e., metal *N*-benzoylphenylhydroxylaminates can be arranged in the following sequence (polarographic spectrum)[71]: Cu(II) < V(V) < Tl(I) < Bi(III) < Fe(III) < Pb(II) < Cd(II) < Mo(VI) < W(VI) < Ga(III). In some cases the values of $E_{1/2}$ for metal ions in the aqueous medium are very close, while in organic solvents they differ significantly. Thus in an aqueous medium the values of $E_{1/2}$ for the copper(II)–bismuth(III), indium(III)–cadmium(II), copper(II)–lead(II), copper(II)–cadmium(II), and indium(III)–lead(II) systems are less than 0.1 V which makes it difficult to determine the above components in mixtures.

The application of extraction polarography makes it possible to determine certain elements when these are present jointly. For example, in a benzene extract the values of $\Delta E_{1/2}$ are as follows: 0.19 V for copper(II) and bismuth(III), 0.29 V for copper(II) and lead(II), 0.30 V for copper(II) and cadmium(II), 0.13 V for lead(II) and thallium(I), 0.30 V for indium(III) and cadmium(II), 0.35 V for indium(III) and lead(II), and 0.48 V for indium(III) and thallium(I). A similar observation has been made for extracts in isopentyl alcohol and ethyl acetate. The values of $E_{1/2}$ in these solvents are sufficient for the joint polarographic determination of the above pairs of ions even when one is present in a considerable excess. The possibility of the polarographic determination of molybdenum in the presence of other metals after extraction of its BPHA complex with chloroform has been noted[39].

The results of the polarographic study of *N*-cinnamoylphenylhydroxylamine (CAPHA) and its metal complexes have been published[72–81]. In organic solvents CAPHA is reduced at −1.2 V relative to the saturated calomel electrode, so that the limit of the polarographic determination is 0.0 to −1.2 V. The CAPHA complexes of thallium(I), lead(II), copper(II), cadmium(II), zinc(II), nickel(II), iron(III), gallium(III), bismuth(III), indium(III), titanium(IV), vanadium(V), zirconium(IV), tungsten(VI), and molybdenum(VI) have been investigated in pentyl alcohol, ethylacetate, benzene, and chloroform with added methanol.

The dependence of the height of the wave for the copper, indium, and iron complexes of CAPHA in the benzene extract on the initial metal concentration in aqueous solution is linear and indicates the possibility of the determination of these elements by the extraction-polarographic method. Since this entails an increase of the selectivity of the elements as a result of the different polarographic behaviour of the CAPHA complexes of metals in organic solvents, indium(III) can be determined in the presence of copper(II) and lead(II) and in mixtures with cadmium(II) and gallium(III), copper(II) can be determined in the presence of bismuth(III), thallium(I) can be determined in the presence of indium(III) and gallium(III), etc. Furthermore, the selectivity of the determination increases owing to the unequal capacities of the metal complexes of CAPHA for extraction under the conditions of different acidities of the aqueous solution. Thus the lead, zinc, nickel, and cadmium complexes are not extracted μat pH 3 and in the extraction polarographic method do not therefore interfere in the determination of molybdenum, tungsten, gallium(II), iron(III), titanium(IV), vanadium(V), and indium. It is possible to determine indium and copper in the presence of various elements.

It has been observed that metal *N*-cinnamoylphenylhydroxylaminates give rise to the following polarographic spectrum in benzene extracts in terms of their ability to be reduced at the m.d.e.: Cu(II) < Tl(I) < Bi(III) < Mo(VI) < V(V) < Fe(III) < Cd(II) < Pb(II) < W(VI) < Ti(IV) < In(III).[74] By introducing tartaric acid and sodium fluoride into the aqueous phase before extraction, the interfering influence of tin, vanadium, titanium, molybdenum, and iron is eliminated. An extraction-polarographic method has been developed on the basis of experimental studies for the determination of copper and lead in various materials; it is distinguished by a high sensitivity and a fairly high selectivity[74].

Various oxime derivatives have found applications in extraction polarography[83–85]. The possibility of the extraction-polarographic determination of microgram amounts of nickel after its concentration in the form of the dimethylglyoximate has been investigated[85]. The method is based on the use of the catalytic hydrogen wave and is therefore one of the most sensitive polarographic procedures for the determination of nickel. When dimethylglyoxime is added to a solution containing nickel, the height of the nickel reduction wave increases by a factor of approximately 6. The lower limit of the determination of nickel under the recommended conditions is 1×10^{-6} M at a m.d.e. and 1×10^{-7} at a stationary mercury electrode. The sensitivity increases appreciably when oscillographic polarography is used (as far as 1.5×10^{-8} M).

A study of the possibility of using α-furylglyoxime and α-benzylglyoxime showed[85] that it is better to employ dimethylglyoxime, since it dissolves more readily than α-benzylglyoxime, and the wave heights do not differ quite so much (in the case of α-furylglyoxime the wave height is much smaller). Copper and cobalt are extracted together with nickel from ammonia solutions in the form of hydroxyquinolinates. Although the extraction is not quantitative, copper and cobalt nevertheless interfere with the photometric determination of nickel. On the other hand, the proposed extraction polarographic method makes it possible to determine nickel quantitatively in the presence of amounts of copper and cobalt in the extract greater by a factor of 100.

Polarographic data for metal *salicylaldoximates and thenoyltrifluoroacetonates* in toluene and benzene extracts and in butanol–acetophenone mixtures have been published[8]. In toluene polarographic waves were observed for copper, iron, cobalt, nickel, palladium, and titanium salicylaldoximates, i.e. a much greater number of metal compounds of this reagent are reduced in toluene than in the case of hydroxyquinolinates[6].

Among the thenoyltrifluoroacetonates (TTA), only copper, lead, thallium, and uranyl complexes are reduced polarographically[8]. This makes it possible to determine copper and lead in the presence of much greater amounts of bismuth, which does not give rise to a wave. The use of isobutyl methyl ketone (IBMK) as the extracting solvent makes it possible to include iron ions among those of the elements investigated[100]. When iron(III) is extracted in the form of a complex with TTA, the extraction is carried out from an acetate buffer solution at pH 5.8; a complex anodic-cathodic wave is observed in the organic phase at a potential characteristic of the reduction of $Fe(TTA)_3$, which indicates the presence of iron(III) and iron(II) complexes in the organic phase. A polarographic determination of thallium(III), which is difficult to determine in aqueous media, is also possible.

TTA is unsuitable for extraction polarography as a result of the narrow range of polarisations. With increase of the acidity of the medium, the comparatively narrow range of m.d.e. cathodic polarisations (−0.20 – −0.75 V) becomes narrower still (is reduced to −0.60 V).

Phosphorus dithio-acids are widely used as analytical reagents in separations by the extraction method, mainly with spectrophotometric detection. However, not all complexes formed by phosphorus dithio-acids with metal ions absorb in the accessible region of the spectrum. This imposes certain limitations on extraction-photometric determinations. Extraction polarography is more promising in such cases. There are few literature data concerning the use of this method for the determination of metals in the form of dithiophosphate complexes. The polarographic properties of a number of transition and non-transition metal diethyl dithiophosphates and their extractability by certain aromatic hydrocarbons have been investigated[26,27,29]. Under the conditions used, the electrochemical reduction of thallium, lead, and copper diethyl dithiophosphates is inhibited by the reduction product adsorbed on the electrode[29].

Diethyl dithiophosphate complexes in another group, including vanadium(IV), chromium(III), nickel(II), cobalt(II), zinc(II), manganese(II), and cadmium(II) compounds, are reduced with fnrmation of waves uncomplicated by adsorption phenomena[29], which is due primarily to the fact that the reduction occurs in the range of potentials more negative than the electrocapillary zero potential[29].

Dithiocarbamates are used in extraction-polarographic analysis mainly for the determination of elements which do not form coloured complexes and which cannot be determined spectrophotometrically.

The extraction of lead(II) by benzene in the form of $Pb(R_2NCS_2)_2$ and $Pb[(CH_2)_nNCS_2]_2$ ($R = C_2H_5$ or C_4H_9; $n = 4, 5$) has been investigated polarographically. The distribution of the chelates between water and the organic phase was followed by oscillographic polarography[55]. The presence of nickel(II), chromium(III), zinc(II), aluminium(III), molybdenum(VI), tungsten(VI), vanadium(V), and titanium(IV) in the test solution does not interfere with the determination of lead(II), because the chelates of the first four metals are reduced at more negative potentials than $Pb(R_2NCS_2)_2$; the chelates of the remaining elements are hardly extracted at pH >7. The high resolving power of oscillographic polarography makes it possible to determine lead(II) in the presence of comparable amounts of bismuth(III) and thallium(I).

Taking into account data for the extraction of zinc(II) as $Zn(R_2NCS_2)_2$ by pentyl acetate at pH 3, a method has been developed for the extraction-polarographic determination of zinc(II) in the blood of animals[55]. The concentration of zinc(II) was found from the limiting current for the wave with $E_{1/2} = -1.45$ V (relative to s.c.e.). In order to eliminate the interference by cobalt(II) and manganese(II), sodium thiosulphate was added. The optimum conditions for the distribution of $Zn(R_2NCS_2)_2$ in the benzene–water system obtain at pH 10–11.

The possibility of the selective extraction of copper(II), lead(II), zinc(II), manganese(II), cadmium(II), nickel(II), and bismuth(III) in the form of their dithiocarbamate complexes has been investigated[52]. Best results are achieved in in a 1:1 benzene–methanol medium (an emulsion is formed in toluene). The values of $E_{1/2}$ for these complexes are similar. In order to determine the metal ions present jointly in the same solution, use was made of extraction at different pH in conjunction with masking reagents.

Other aspects of the electrochemical behaviour of metal chelates in relation to derivatives of dithiocarbamic, xanthic, and dithiophosphoric acids were discussed in detail in previous sections of the review.

Dithizone is used to a lesser extent as an extractant in extraction polarography. A method has been developed for the determination of copper in natural waters based on the concentration of copper by extraction in the form of a dithizonate and the polarography of the toluene extract in the presence of a hydrochloric acid buffer solution as the supporting electrolyte[38].

Extraction polarography can prove to be irreplaceable in those cases where the technological processes are carried out in non-aqueous media, for example in polymerisation in the presence of catalysts. The concentration of a copper catalyst has been determined[99] directly in the reaction mixture. In such cases re-extraction is impracticable in view of the long duration and laborious nature of the operations, and extraction polarography therefore significantly simplifies and facilitates analysis.

Among different electrochemical analytical methods, particular interest attaches to anodic extraction voltamperometry at solid electrodes, which involves a preliminary extraction of the complexes into a diluent and the measurement of their oxidation current. In a 2:3 toluene–acetone mixture in the presence of 0.1 M $LiClO_4$ supporting electrolyte chromium(III), manganese(II), iron(III), cobalt(II), cobalt(III), nickel(II), copper(II), zinc(II), cadmium(II), lead(II), bismuth(III) and thallium(I) dithiocarbamate, xanthate, and dithiophosphate complexes are oxidised at graphite and platinum disc electrodes with formation of diffusion waves whose positions along the potential axis are determined by the nature of the central ion and the ligand[57–59]. The results make it possible to select the extractant as a function of the object of the analysis. For example, in the determination of nickel(II) and zinc(II) extraction should be carried out with dithiocarbamates, since the dithiophosphate complexes of the above metals are oxidised virtually at the same potential (1.13 and 1.08 V respectively). In extraction from strongly acid media preference should be given to dithiophosphates. Account must be taken also of the electrode. In the oxidation of dithiophosphate complexes at a platinum electrode no waves were observed on voltage–current curves.

Anodic voltamperometry makes it possible to extend the range of extracting solvents compared with polarography. Apart from toluene, chloroform and carbon tetrachloride have been used in the determination of copper(II).[48,59] The extraction of metal dithiocarbamates by these solvents has been thoroughly investigated[108]. However, their use in polarography encounters difficulties owing to the narrow range of cathodic polarisation potentials. The oxidation of copper(II) dithiocarbamate at graphite in mixtures of acetone with $CHCl_3$ and CCl_4 gives rise to a single distinct diffusion wave at a potential of 0.6 V. The oxidation current at a rotating electrode in a 2:3 carbon tetrachloride–acetone mixture is several times higher than in a 2:3 toluene–acetone mixture at the same concentration. The lower limit of the detection of copper(II) is 0.5 – 0.7 μg ml^{-1}.[59]

Anodic extraction voltamperometry has a somewhat higher detection limit than polarography; the error of the determination is also increased (from 3–6% to 8–12%). Nevertheless this method also has undoubted advantages. Firstly, mercury as the electrode material is eliminated. Secondly, the duration of analysis is greatly reduced, because there is no need to remove the dissolved oxygen from the electrolyser (this is particularly important in routine analyses). Finally, it is possible to eliminate highly toxic solvents such as benzene and its analogues.

Together with the extraction of inner complexes, procedures based on the extraction of elements into an organic solvent in the form of thiocyanate complexes[109] or metal halide acids[22,32,110,111] have become common in voltamperometry.

In the determination of antimony and arsenic in industrial objects, they were extracted with benzene in the form of bromide complexes[112] and the extracts were polarographed in

a LiCl solution in ethanol or glacial acetic acid as the supporting electrolyte. The oscillopolarogram of the arsenic(III) extract shows two peaks at potentials of −0.3 and −0.8 V (relative to the mercury at the bottom of the cell). The second peak is suitable for the determination of arsenic(III) in the presence of antimony and tin in proportions of 1 : 100. In these supporting electrolytes antimony(III) is reduced at a potential of −0.2 V with formation of a distinct peak. Antimony(III) has been determined in objects free from arsenic(III).

Among the new extractants used for concentration and determination mention should be made of α-dibutylphosphinyl-α-hydroxypropionic acid (DPHP) with added isopentyl alcohol. This system has been recommended for the determination of cadmium(II) on the basis of the limiting current for the reduction of its complex with DPHP in the presence of copper(II).[101] The reaction of copper(II) with DPHP is masked by the addition of ethylenediamine.

The conditions for the extraction of indium(III) and tin(IV) ionic association complexes with tri-n-octylamine (TOA) in dichloroethane and the polarography of the extract in methanol in the presence of NH_4Br as the supporting electrolyte have been used to determine indium and tin in the $CdSiAs_2$ semiconducting compound alloyed with indium[102]. The change in the TOA concentration from 0.25 to 1.25 M increases the percentage extraction of indium from 54 to 99%. The composition of the extracted ionic association complex $(TOAH)_2SnCl_2$ was determined from the bilogarithmic plot of the partition coefficient against the amine concentration. A lower limit of $(2–5) \times 10^{-8}$ M in the detection of the indium impurity in $CdSiAs_2$ has been achieved as a result of a combination of extraction by concentration with polarographic accumulation of indium[103].

The principal results of the extraction-polarographic determinations of metals in various objects are summarised in Table 3. The Table does not include the results of studies involving re-extraction before polarography[113–116].

Table 3. Extraction-polarographic determination of elements in various objects.

Element	Reagent	Object of study	Conditions of extraction-polarographic determination	Remarks	References
Copper	8-hydroxy-quinoline	alloyed steels, babbitts	pH 3–14, toluene : methanol = 2 : 3; supporting electrolyte—0.1 M LiCl; Fe^{3+} ions masked by sodium fluoride	measurable concentration limits 4×10^{-6}–5×10^{-5} M	6,10
Copper	8-hydroxy-quinoline	petroleum	pH 2.4–12.0; benzene : methanol = 1 : 1; supporting electrolyte—NH_4NO_3 + NH_4SCN; accumulation potential = –0.4 V	relative error of extraction-polarographic determination 5.6%	17
Copper	dithizone	natural waters	extracted with 0.001% solution of dithizone in toluene at pH 2.15; polarographed mixture: toluene–acetone–hydrochloric acid buffer (1 : 19 : 5)	wave height proportional to concentration in the range 1×10^{-6}–8×10^{-5} M; 0.12 mg litre^{-1} determined in the water of Belaya River with a relative error of 3.7%	38
Copper and lead	CAPHA	silts and natural waters	pH 5.6–6.0; benzene (chloroform) : methanol = 2 : 3; supporting electrolyte—0.1 M LiCl	limits of proportionality of i_{lim} for a lead complex 1×10^{-5}–6×10^{-4}M and for a copper complex 1×10^{-5}–8×10^{-4} M; Ni, Co, Zn, Mn, In, Ga, Fe, and Cd do not interfere with determinations; sensitivity 5×10^{-4}% in silts and 10 mg litre^{-1} in water; relative error not exceeding 5%	74
Copper and lead	CAPHA	sedimentary rocks and minerals	pH 5.6–7.7; benzene : methanol = 2 : 3; supporting electrolyte—0.1 M LiCl	simultaneous determination based on difference in $E_{1/2}$ ($\Delta E_{1/2}$ = 0.25 V); sensitivity of method 5×10^{-4}%; relative error not exceeding 5%	73
Lead	sodium dialkyl-dithiocarbamates	heat resistant EI-437B nickel alloy	pH 8.5; benzene : ethanol = 2 : 3; supporting electrolyte—0.1 M $NaClO_4$	upper limit of proportionality 7×10^{-4}M (R = C_2H_5) and 1×10^{-3} M (R = C_4H_9); Ni, Cr, Zn, Al, Mo, V, Ti, Bi, and Tl do not interfere with determination; lower limit of determination 1×10^{-6} M (oscillopolarography)	55
Lead	8-hydroxy-quinoline	–	pH 9–12; extractant—fused naphthalene; supporting electrolyte—0.1 M pyridine + 0.1 M $HClO_4$; extract dissolves in dimethyl-formamide	limits of calibration graph 0–112 μg/10 ml; Pd, Cd, and Hg interfere with determination	61
Lead and zinc	xanthates	standard specimens and industrial objects	pH 3–5; extractant—benzene (CCl_4 or $CHCl_3$); supporting electrolyte—LiCl in ethanol	tenfold amounts of Fe, Ni, and Cu interfere with determination (oscillopolarography)	86
Zinc	sodium diethyl-dithiocarbamate	animal blood	pH 3; pentyl acetate : ethanol = 2 : 3; supporting electrolyte— 0.2 M $NaClO_4$; optimum conditions for zinc: benzene–ethanol at pH 10–11	interference by Co and Mn is eliminated with sodium thiosulphate; lower limit of determination 8×10^{-6}M	55
Iron, manganese, and zinc	sodium dimethyl-dithiocarbamate, ethylenebis-dithiocarbamate	residual amounts of ferbam, ziram, and maneb	benzene : methanol = 2 : 3; supporting electrolyte—0.2 M $LiClO_4$	lower limit of determination for Fe and Mn 1×10^{-7} M (a.c. polarography)	23
Iron	acetylacetone, thenoyltrifluoro-acetone	–	extractant—isobutyl methyl ketone; supporting electrolyte—0.1 M $(C_4H_9)_4NClO_4$; pH 8.8–9.1	quantitative extraction with acetylacetone; iron can be determined in the concentration range 8×10^{-5}–1×10^{-3} M	96

Table 3 (contd.)

Element	Reagent	Object of study	Conditions of extraction-polarographic determination	Remarks	References
Nickel	dimethylglyoxime	sea water	pH 9-10; ammonia buffer solutions; polarographed mixture: toluene—1 M ammonia buffer-ethanol	down to 1×10^{-8} M Ni determined from catalytic hydrogen wave; hundred-fold amounts of Cu and Co in extract do not interfere (oscillographic differential polarography)	85
Indium	4-benzoyl-3-methyl-1-phenyl-5-pyrazolone	doped semiconducting alloys	pH 1.2-1.3; polarographed mixture: chloroform—1 M LiCl or 0.75 M NH_4Br in methanol (1:4)	sensitivity of determination much higher when NH_4Br is used than for LiCl; accompanying elements (Cd, Sb, As) do not affect peak height	94
Indium	8-hydroxyquinoline	–	extractant—fused naphthalene; pH 3-12; supporting electrolyte—0.1 M pyridine + 0.1 M $HClO_4$ in dimethylformamide	i_{lim} proportional to metal concentration in the range 0.7-21.5 $\mu g\ ml^{-1}$; error of determination 1.1% majority of cations and anions do not interfere with determination; complexone III interferes	62
Molybdenum	8-hydroxyquinoline	alloys and other complex materials	extractant—naphthalene; extraction temperature ~ 60 °C; pH 2.25-5.30; supporting electrolyte—0.1 M $NaClO_4$ + 0.1 M $HClO_4$ in DMF	citrates, oxalates, tartrates, $PdCl_2$, and $FeCl_3$ interfere with determination; the majority of ions do not interfere	
Molybdenum	BPHA	steel	Mo extracted from hydrochloric acid solution with 2 ml of 1% BPHA solution in $HClO_4$; LiCl in methanol also added	the majority of metals and complex-forming substances do not interfere with determination	39
Cadmium	α-dibutylphosphinyl-α-hydroxypropionic acid	aluminium alloys	isopentyl extract polarographed in the presence of 0.1 M LiCl in ethanol as supporting electrolyte; pH of aqueous phase 6	minimum measurable amount of cadmium 5.6×10^{-4} mg ml^{-1}	101
Antimony	diantipyrinylmethane	steels	1 M LiCl in ethanol added to extract before oscillopolarographic measurements	linear relation between peak height and Sb^{3+} concentration holds between 1×10^{-7} and 1×10^{-3} M; Cu for a 20:1 ratio, Bi for a 3:1 ratio, and Sn for all ratios interfere with determination; relative error <10%	92
Arsenic	–	steels	As^{3+} extracted from 11.5 *N* HCl with carbon tetrachloride and butanol is added	error +0.4-2.0% (oscillopolarography)	96
Gallium	salicylic acid	metallic aluminium	pH 3; homogeneous mixture; butyl acetate–aqueous 0.5 M LiCl solution and 0.1 M sodium salicylate—ethanol (1:1:2)	range of proportionality of gallium concentration 5.4×10^{-4}-2.2×10^{-3} M	97

*Extraction in the form of halide complexes.

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