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Present and Future Status of
Organic Analytical Reagents—Part III

ORGANIC ANALYTICAL REAGENTS IN ELECTROANALYSIS

(Technical Report)

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Present and future status of organic analytical reagents—Part III: Organic analytical reagents in electroanalysis

Abstract - This report indicates the various applications of OAR in electroanalysis. Since it is not possible to show all applications in the literature, some pioneering papers as well as selected only recent publications and reviews are cited. It must be emphasised that there is an increasing interest in the field, particularly where the electrochemical properties of OAR are used for modification of electrochemical reactions at electrodes.

INTRODUCTION

Two aspects can be distinguished in the application of organic analytical reagents (OAR) in electrochemical methods:

- the general influence on the medium and conditions, in which the electroanalytical technique of determination is applied,
- the active participation of the OAR in the electrochemical processes on which the determination is based.

This division into two groups is to some extent arbitrary as the functions of OAR may, at least, in some instances be included in both classes. The first group of applications will be mentioned only in a rather general way, as they are usually not specific to electroanalytical procedures per se. Within this group the following types of organic reagents, or rather organic substances, can be distinguished:

- 1) organic solvents, and substances used to modify the physical properties of the medium,
- 2) components of pH and pM buffers and background electrolytes,
- 3) general masking reagents, used to prevent undesirable reactions which may interfere - physically or chemically - with the electroanalytical determination, and
- 4) other organic compounds used e.g., in reference electrodes.

The second group is specific to electroanalytical methods, they consists of the following types of substances :

- 1) titrants, which only participate in the chemical reaction under given conditions and those which, when present in excess, after the end-point, undergo an electrochemical reaction, or which form an electrochemically active complex with the analyte.

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- 2) components of background electrolytes, which directly or indirectly react with the analyte forming electrochemically active species whose properties are utilised for analyte determination,
- 3) compounds, which influence the electrochemical process making possible determination, of the analyte,
- 4) compounds, used as essential components of electrochemical sensors or which modify their properties, thus permitting application of the sensors in selective procedures.

The above classification does not include complex organic compounds with biochemical activity such as enzymes, which may formally be also treated as organic reagents. However their application, conditions of analytical procedures and general properties distinguish them in principle from the types of OAR enumerated and therefore requires separate treatment.

OAR USED TO MODIFY THE MEDIUM CONDITIONS

1. Organic solvents, and substances used to modify the physical properties of the solvents

Organic solvents are not always considered as OAR, however, for the sake of completeness and because it is difficult to give a very clear distinction of substances defined as reagents or otherwise some discussion is needed. Organic solvents play special roles in electroanalysis (1,2) as follows:

(a) Shifting of the position of chemical equilibria compared to that which pertain to aqueous solutions.

This is most commonly encountered in protolytic equilibria where the specific solvation effects and acid-base properties of the solvent modify the reaction course. These effects are of importance in potentiometric, coulometric, conductometric or high-frequency titrations of weak organic acids or bases (3-5) where the differentiating or leveling effects of the solvents are exploited. For these purposes the following solvents are commonly used: aliphatic acids (e.g., acetic acid, formic acid, trifluoroacetic acid, propionic acid), ketones (e.g., acetone, methyl isobutyl ketone, methyl ethyl ketone), glycols (e.g., ethylene glycol, propylene glycol), amines (e.g., ethyle- nediamine, benzylamine, butylamine, pyridine), and others (e.g., dioxane, dimethyl sulphoxide, tetrahydrofuran, dimethylformamide, acetonitrile). A well-known group of solvents, so called "G-H solvents", being mixtures of glycols and aliphatic alcohols are also often used (6).

The shifts of the chemical equilibrium in precipitation reactions are usually connected with the decrease of the solubility of products in less polar media, e.g., methanol, ethanol or acetone. These solvents are used in titration of inorganic ions which form precipitates of moderate solubility (e.g., PbSO_4 , AgCl) using potentiometric or amperometric end-point detections (7,8). Common solvents are alcohols, acetic acid, 1,4-dioxane and trifluoroacetic acid usually mixed with water.

Organic solvents except for acetic acid, acetonitrile, dimethylformamide (11) are rarely used as media for redox titrations performed with potentiometric or voltammetric detection. The reason is probably that of the lack of knowledge of solvation processes in complicated systems such as those encountered in redox titrations (9,10).

Potentiometric compleximetric titrations in acetonitrile do not offer special advantages over those carried out in water (12).

(b) Extension of the accessible potential range can be achieved with non-aqueous solvents which are more difficult to be oxidized or to be reduced than water (13). The practically accessible potential range also depends on the supporting electrolytes used. Perchlorates, fluoroborates and fluorophosphates of alkali metals or of tetraalkylammonium cations are commonly used (14). For example, in acetonitrile the potential range extends to values as low as -3.15 V (measured vs. ferrocene / ferricinium reference electrode) with LiClO_4 and up to $+3.20$ V (vs. ferrocene / ferricinium) with $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ as supporting electrolyte (15,16). In tetramethylene sulfone the accessible potential range with LiClO_4 extends from -3.55 to $+2.4$ V (vs. ferrocene / ferricinium) or even to $+3.40$ V with $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ (15, 17). Few applications in inorganic analysis have been described, apart from those for the determination of alkali, alkaline and rare earth metals (18).

The non-aqueous solvents are used in coulometry, especially for coulometric titrations, in numerous cases to extend the potential range (8). Useful examples include acid - base titrations in acetic acid, its anhydride or their mixtures, acetonitrile, acetone, ethylene glycol, *m*-cresol, aliphatic alcohols, acids, amines and dimethyl sulfoxide. For redox titrations solvents are used which exhibit stability against reduction or oxidation. The most common media are acetic acid and dimethylformamide, as well as methanol, 2-methoxyethanol, diethylene glycol monomethyl ether as solvents and pyridine, 2,2'-iminodiethanol, imidazole as solvents for the Karl Fischer determination of water (19, 20).

(c) In liquid-state ion-selective electrodes and in electrochemical investigation of phenomena at the Interface between Two Immiscible Electrolyte Solutions (ITIES) a number of organic water immiscible solvents have been used. As their polarity varies significantly the partition of the ionophores between water and solvent also changes, key examples being nitrobenzene (21) and dichloroethane (22), two solvents of widely differing polarity. For the preparation of liquid-state membranes similar solvents can be used but more commonly 2-nitro-*p*-cymene (23) and *o*-dichlorobenzene (24) are used. In the preparation of PVC membranes for ion-selective electrodes (25) tetrahydrofuran and cyclohexanone are used as solvents with the addition of a variety of plasticizers (mediators) for the improvement of both mechanical and electrochemical properties of the prepared membranes. *p*-Nitrophenyl octyl ether (e.g., in nitrate electrode), *o*-nitrophenyl phenyl ether (e.g., in lithium electrode), dioctyl phenylphosphonate and decanol (e.g., in calcium and divalent-ion electrodes respectively), tris-(2-ethylhexyl) phosphate (e.g., in ammonium electrode), tributyl

phosphate or dibutyl phthalate or diphenyl ether (e.g., in potassium electrode) serve as examples of the great number of reagents of similar structures differing by substituents which are used by individual scientists or by commercial producers of electrodes (21).

Beside PVC some other polymers have been used as matrices for electrodes containing liquid ion-exchangers for example carboxylated PVC (26), poly(methyl acrylate) (27), epoxy resins (28) and a natural polymer Urushi (29). Polymerisation carried out in the presence of compounds having properties of liquid ion-exchangers, cause their chemical incorporation into the sensing material (30,31).

2. pH and pM buffers and supporting electrolytes and depolarizers

The pH buffers containing organic components are widely used in electro-analytical techniques (32). Beside their usual role the complexing properties of buffer components are also very often used for masking interfering ions, or for preventing undesirable reactions of the components of the analytical sample. When such buffers are used it is important to ensure that they are not electrochemically active in the potential range of interest. It should be noted that some are resistant only against oxidation, and others against reduction. The proper choice of a buffer and supporting electrolyte enables study or determination of species which are electrochemically active in the extended potential range. Most of the commonly used pH buffers contain formic acid, acetic acid, succinic acid, phthalic acid, hexamethylenetetramine, aminoacetic acid, tris(hydroxymethyl)aminomethane, tartaric acid, oxalic acid, citric acid and many polyaminopolycarboxylic acids which, at the same time, can serve as masking agents for metals.

Substances forming complexes of fairly low stability with metal ions and with their buffering range not far from biological relevance include (33,34) piperazine-1,4-bis(ethanesulphonic acid) (PIPES), 3-[tris(hydroxymethyl)methylamino]propane sulphonic acid (TAPS), 2-(carbamoylmethylamino)ethane sulphonic acid (ACES), 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulphonic acid (HEPES), 3-morpholinopropanesulphonic acid (MOPS) which have been suggested as suitable buffer components in blood electrolyte measurements with ion - selective electrodes (35).

Strongly metal complexing substances are used as components of so called "metal buffers" (32,36). Because of the protolytic properties of most of the metal buffer components, the pM values produced by such buffers are pH dependent and therefore require control. The main analytical use of pM buffers is for calibration of ion-selective electrodes.

All pH buffers mentioned above are often used as supporting electrolytes in electroanalytical measurements (1). Organic salts are also used for this purpose especially in organic (or mixed) solutions. For example, in controlled potential coulometry (18) tetraethylammonium perchlorate for determination of Li, Na, Sm, Eu in acetonitrile or methanol. The corresponding bromide or iodide salts are used for determination of ytterbium and barium. Such substances are used as supporting

electrolytes in voltammetric techniques as they are not reduced in the potential range in which the substances to be determined undergo electrochemical reactions. In some cases special reagents are added as depolarizers, among which hydroquinone, pyrogallol, *m*-cresol, urea and aliphatic alcohols have been used (8).

3. General masking substances

One of the main applications of masking substances in electroanalytical chemistry is to prevent undesirable reactions under the conditions of the determination. These reactions are mainly precipitation of metal hydroxides at higher pH values. In this aspect many buffers can be used, provided they contain substances which complex the concomitants including the main sample component. Due to complexation the half-wave potential of the analyte or of the interferent may be shifted. These shifts are necessary, when in non-complexing media, the half-wave potentials of several species present in the sample including the analyte are similar.

Tables of polarographic half-wave potential values in the presence of organic masking reagents are available (37,38), indicating the effects of complexation. In the case of reversible systems this is simply calculated from the stability constants and the equation for the half-wave potential. The most commonly employed organic complexing agents are: oxalate, tartrate, citrate, ethylenediamine, 2,2',2''-iminotriethanol, 4,5-dihydroxybenzene-1,3-disulphonate (Tiron), nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), cyclohexane-1,2-diaminetetraacetate (CDTA), diethylenetriaminepentaacetate (DTPA), [(ethylenedioxy)diethylenedinitrilo]tetraacetate (EGTA), N-carboxymethyl-N'-(2-hydroxyethyl)ethylenediiminodiacetic acid (HEDTA), triethylenetetraminehexaacetate (TTHA). An excellent example illustrating this behaviour is the determination of Fe and Cu in the presence of 2,2',2''-iminotriethanol (39). In the absence of this ligand the ions are reduced close to 0.00 V (vs.SCE), while in its presence copper is reduced at -0.50V and iron at -1.05V. The same ions may be also individually reduced in the presence of EDTA at pH 5 (40).

The determination of zinc(II) in presence of nickel(II) and cobalt(II) in excess is possible in nitrilotriacetate at pH 9, while in its absence zinc(II) is reduced at more negative potentials than the accompanying metals and thus cannot be determined (41). The typical mutual interference of cadmium(II) and indium(III) in various non-complexing electrolytes can be avoided when EGTA or DTPA are added (42). In certain cases the addition of a masking agent may completely shift the reduction wave beyond the accessible potential range, making possible determination of traces of weakly complexed ions in presence of the excess of masked metal. Thus in a TTHA solution indium(III) does not give its reduction wave enabling determination of many of the metallic impurities in indium (43).

Sulphosalicylic acid has been used with advantage when zinc(II) and iron(II) are to be determined in presence of excess aluminium, to prevent precipitation of aluminium(III) hydroxide and to shift the

reduction waves of both analytes (44). Similarly in anodic stripping determination of silver(I) in the presence of excess of copper(II), NTA reacts so strongly with copper(II) that the determination of silver(I) is possible (45). EDTA can effectively mask lead(II) and cadmium(II) in the anodic stripping voltammetric determination of thallium(I) (46). The role of EDTA is also important in the determination of sulphide by differential pulse polarography where it masks metal traces and thus prevents catalytic oxidation of sulphide (47).

So called ionic strength buffers or adjustors for the creation of optimal conditions in potentiometric measurements often contain organic reagents as masking or demasking agents. The best known example is the "Total Ionic Strength Adjustment Buffer" (TISAB) used in fluoride measurements, which serves for pH buffering and for decomplexation of fluoride initially bound with such metal ions as aluminium(III) or iron(III). Such TISAB solutions may contain citric acid (49), CDTA (48) or tiron (50). Another example is the Constant Complexation Buffer which in the potentiometric determination of calcium(II), provides a constant complexation level of calcium(II) by addition of iminodiacetate and thus eliminates the interference from hydrogen carbonate and sulphate (51). The interference of magnesium on calcium is diminished by addition of acetylacetone. In the potentiometric determination of sulphide the "Sulphide Anti-Oxidant Buffer" (SOAB) is used, which contains salicylic acid and ascorbic acid to complex metal ions and to prevent analyte oxidation (52).

4. Other organic reagent systems

Organic reagents are increasingly used in reference electrodes.

Ferrocene (bis-(η -cyclopentadienyl)iron(II)), cobaltocene (bis-(η -cyclopentadienyl)cobalt(II)), and bis(biphenyl)chromium(I) tetraphenylborate should be mentioned for use in establishing the Solvent Independent Reference Electrodes (SIRE) (53).

Quinhydrone as well as chloroanil are classical substances used in pH electrodes (54,55). Metal acetates are used as electrolytes in reference electrodes used in non-aqueous or mixed solutions which contain acetic acid.(56). Such systems are also used in electrolytic bridges.

OAR AS ACTIVE PARTICIPANTS OF THE ELECTROCHEMICAL PROCESS

1. OAR as titrants

There is a vast number of OAR used as titrants in titrations with electrochemical end point detection. It is not possible herein to give a complete survey and only most common representatives or particularly interesting substances of different types will be mentioned. The titrants will not be separated into groups according to the technique of detection because especially for "inert" titrants it is not critical which technique (potentiometric, amperometric, biamperometric) has been used. The determination is based on the chemical reaction in the solution and the availability of a suitable detection system. The end-point of the titrations are mainly based on the observation of the

change of the metal ion concentration in solution. More interesting are examples where the titrant is electroactive and its excess is oxidized or reduced electrochemically giving the analytical end-point signal. In some titrations metal complexes are used as end-point indicators. For example when polyaminopolycarboxylic acids are used as titrants with potentiometric end-point detection with mercury and silver ions, the electrode may be considered as an electrode of the first and the second kinds, respectively, indicating the concentration of the chelating agents (57-59).

One of the ways of using the ligand effect in titration procedures with voltammetric end point detection is shifting of the potential of anodic oxidation of the metal, especially mercury, at mercury indicator electrode (60). This effect can be also employed indirectly for the determination of a number of ions on the basis of metathetic reactions. Various reagents have been used as titrants (61-63) and some typical examples are summarized in Table 1.

Table 1. Examples of most common organic titrants used in electroanalytical procedures.

Titrants, examples	Analytes	Detection	Ref.
A. Complexing reagents			
Polyaminopolycarboxylic acids			
EDTA	most metal ions	pot	64-68
EGTA		amp	69-71
		biamp	72
HEDTA		pot	64
		amp	73-75
DTPA		pot	64
		amp	76
TTHA		amp	42, 75
		amp	42, 77
CDTA		pot	78
NTA	amp	79	
		pot	64, 66
Polyamines			
TRIEN	transition metals	pot	64
TETREN		amp	76
		pot	64
Others			
<i>N</i> -benzyliminobis(methyl- phosphonic) acid	Cu	pot	80

Table 1 (contd)

Titrants, examples	Analytes	Detection	Ref.
B. Precipitate-forming reagents			
Chelating agents			
Dithiocarbamates	Cu, Cd, In, Ni, Pb, Zn	pot	64
	Hg	amp	81
	Mn	biamp	82
<i>N</i> -(2-naphthyl)- -mercaptoacetamide	Ag, Bi, Cu, Hg, Sb	amp	84
	Ag	biamp	85
Dithioamide	Ag	pot	6
Thioacetamide	Ag, Bi	pot	64, 83
	Cu	amp	86
Thiourea	Ag	pot	87
Mercaptobenzothiazole	Ag	pot	88
	Ag, Pd	amp	88, 89
<i>N</i> -Benzoylphenylhydroxamine and its analogues	Ga, Ce, Th, Ti, Zr	amp	90
Dimethylglyoxime	Ni	amp	91, 92
Non-chelating agents			
Tetraphenylborate Na	Cs, K, Rb	pot	64
	K	amp	93, 94
C. Redox titrants	reductants or oxidants	pot., amp., biamp	64, 69
Ascorbic acid			
Hydroquinone			
Chloramine T			
Co, Pb acetates			
2,6-Dichloroindophenol			
D. Acidic titrants	bases	pot	3
Methanesulphonic acid			
Ethanesulphonic acid			
<i>p</i> -Toluenesulphonic acid			
Diphenyl hydrogen phosphate			
Trifluoromethanesulphonic acid			
Benzenesulphonic acid			
E. Basic titrants			
Tetrabutylammonium hydroxide	acids	pot	3
Hexadecyltrimethylammonium hydroxide	acids	pot	3
Alkali metal alkoxide	acids	pot	3
Cyclohexylamine	acid chlorides	pot	95
Lithium aluminium amides	alcohols	pot	3
1,3-Diphenylguanidine	acids	pot	1
1,1,3,3-Tetramethylguanidine	acids	pot	1

In several coulometric titrations the organic reagents are generated electrolytically. Only reagents used as their precursors will be mentioned. The most commonly used titrant is the EDTA complex of Hg^{II} which undergoes reduction at a mercury electrode with liberation of the free ligand (96), or the EDTA complex of iron (III), which when reduced at a platinum electrode, forms a very weak complex of iron (II) acts as a substitution reagent towards many metal ions (97). Other ligands can be generated similarly coulometrically (79,98). Also bis-(2-mercaptoethanol)-mercury(II) or the analogous compound of the thioglycolic acid after reduction at mercury cathode sets free ligands which can be used for the determination of Au^{III} , Ag^{I} , Hg^{I} , Cu^{II} , Pd^{II} , Pt^{III} , Pt^{II} (99).

In the titration of some polycyclic aromatic hydrocarbons biphenyl is reduced to its radical, which acts as a reagent for anthracene. benzophenone etc (100).

In the coulometric titration of oxygen the viologen radical cation is used as titrant electrogenerated in the solution of 1,1'-dimethyl-4,4'-bipyridinium dichloride in acetonitrile, dimethylformamide or water (102). For determination of halogens the $\text{I}^{\text{+}}$ ion may be generated in glacial acetic acid from alkyl iodides (101).

2. Reagents for the indirect determination of non-electroactive analytes

This group of OAR consists mainly of substances used in indirect of determinations by voltammetric techniques.

When direct determination of ions which form relatively stable complexes is not possible or difficult because of a very negative half wave potential a complex displacement reaction with an organic chelate is used, e.g., calcium(II) which forms the EDTA complexes of larger conditional stability than zinc. Thus the Zn EDTA complex reacts with calcium ions, the liberated equivalent zinc(II) ions may be easily determined (103). Calcium(II) ion can also be determined via its reaction with Cd EDTA (104). Systems can be selected with respect to pH value and masking agent composition based on the conditional stability constants. Metathetic reactions may be used as in sulphate determination when the precipitated barium sulphate is dissolved in Ag EDTA solution and the equivalent amount of silver(I) ions is determined (105).

Reagents similar to those used in direct titrations are also used for indirect determinations. For a ligand which produces a voltammetric wave at a mercury electrode addition of the sample diminishes the wave, because of consumption of the ligand due to complexation by the determined ion. Examples of such procedures are determination of ($\text{Ca}^{\text{II}} + \text{Mg}^{\text{II}}$) when EDTA is used as ligand, or determination of Ca^{II} only, when EGTA is added in the presence $\text{Na}_5\text{P}_3\text{O}_{10}$ (73).

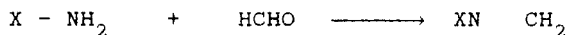
Magnesium ions can be determined based on reduction of 2,2'-dihydroxy-azobenzene(106), Solochrome Violet RS (107), Eriochrome Black T (108) or 8-hydroxyquinoline (109) each of which reacts stoichiometrically

with the metal ions. Similarly the picrolonic acid reaction with calcium ions (110) and that of Pontachrome SW with aluminium ions (111) can be used for the indirect determination of metals.

The presence of organic reagents may also promote a catalytic electrochemical reaction which is of special value when the hydrated ions are reduced at the mercury electrode with significant overpotential. A number of ions may be determined in such a way [Ni^{II}, Co^{II}, Fe^{II}, In^{III}, Ga^{III}, Ti^{IV}, Ge^{IV}, Sn^{IV}], e.g., determination of Fe^{II} and Mn^{II} using thiourea, determination of Ti^{IV} using oxalate or citrate, determination of Ge^{IV} or Sn^{IV} using polyphenols (e.g., pyrocatechol, pyrogallol) (112).

Several organic reagents have been used in adsorptive stripping voltammetry to promote the adsorptive preconcentration of metal complexes at the mercury or at solid electrodes. This technique provides a very sensitive procedure for metals which cannot to be concentrated by formation of amalgams or an elemental metal layer. The usual detection limit is in such procedures in the range from 2×10^{-8} to 10^{-10} mol/l. Useful examples are (113,114): bipyridine for Ni^{II}, catechol for Fe^{III}, U^{VI}, V^V, dimethylglyoxime for Co^{II}, Ni^{II}, cresolphthalexon for Ce^{IV}, Pr^{III}, La^{III}, DTPA for Cr^{III}, Solochrome Violet RS for Ca^{II}, Mg^{II}, Sr^{II}, Ba^{II}, Al^{III} and 8-hydroxyquinoline for Mo^V.

Interesting applications of organic reagents are based on their reaction with the analyte with the formation of an electroactive product. Such procedures are exemplified by the use of formaldehyde in determination of ammonia, amines or amino acids. In the reaction



the products can be easily electrochemically reduced giving a well defined signal (40).

The determination of aldehydes and ketones is based on the formation of semicarbazones or hydrazones which are determined polarographically, in the reaction with semicarbazide (115) or Girard T or D reagent (116, 117) (trimethylammonioacetohydrazide or dimethylammonioacetohydrazide chlorides, respectively).

Ketones react with 2,4-dinitrophenylhydrazine forming the corresponding hydrazones, which after extraction with an inert solvent are determined polarographically in methanolic solution.

Several reagents which are not protolytically active or have weak protolytic properties can be used to enhance the protolytic activity of the analyte. The best known reagents of this type are mannitol, sorbitol (118) and some other polyhydroxy alcohols used in determination of boric acid by potentiometric alkalimetric titration.

2-Aminoethanol is used as absorbent for the carbon dioxide which transforms it into the stronger carbamic acid, and the 2-hydroxyethylammonium ion is then titrated e.g., coulometrically (119-122).

3. Electrochemically inactive surfactants, which influence the electrochemical process

In cases when direct electrochemical determination is impossible or is seriously disturbed by chemical or physical interferences, the addition of small amounts of electrochemically inactive substances may enable the determination, e.g., substances used to suppress polarographic maxima. Examples from the early days of polarography are gelatin, tylose, thymol, adrenaline, methyl green, atropine sulphate, methyl orange and methyl red.

The specific adsorption of organic reagents at the mercury drop electrode influences the rate of the electrode processes as indicated by a shift of the polarographic wave in the negative direction. Irreversible reactions are especially sensitive to such phenomena (123). Some acceleration of an electrode process is also possible which is seen by the shift of the wave towards more positive potentials (124). On this basis procedures have been developed, the so-called electrochemical masking procedures, in which poly(ethylene glycol), Triton X-100, Benex, Aerosol AX, gallic acid, cetyltrimethylammonium bromide, etc. are used as surface active agents in d.c. or a.c. polarography and in inverse voltammetry. In the presence of these substances heavy metal ions such as Tl^I , Pb^{II} , Sn^{II} , Cd^{II} can be determined in the presence of excess of other metals (125-130).

4. Compounds, which are incorporated in an indicator electrode

This group consists of two main types of substances. The first type consists of reagents used for ion-selective membrane preparation. The reagents such as liquid ion-exchangers or neutral carriers responsible for the selective electrode signal are embedded into a polymer matrix or dissolved in a solvent immiscible with water. The second type are reagents used for the modification of electrodes in voltammetric techniques. Such substances must be hydrophobic or they may be chemically bound to the polymeric membrane.

The ionophores used may be ionic substances or neutral species which are able to interact electrostatically or to complex selectively the analyte. Their miscibility with the membrane components is a precondition for the preparation of a stable membrane.

The first group consists of a great variety of compounds used in commercially produced electrodes or reported in research papers. It is impossible to mention all of them but specialized reviews are available (131-140). Only the main types of compounds will be mentioned here, with some representative examples. In many cases reagents used for membrane preparation differ only by the number or size of substituents added to a parent structure giving thus a vast list. With the exception of reagents, which have reached an established position as membrane components, through commercial availability, the choice of substances is arbitrary. The list of organic reagents used as ion-carriers (Table 2) presents examples of the most widely used compounds and includes charged anion carriers, charged cation carriers and neutral carriers.

Table 2. OAR used as ionophores in ion-selective electrodes.

Ion-carrier	Species sensed	Ref.
Anion exchangers		
Quaternary ammonium salts		
trioctylmethylammonium	CO_3^{2-}	141
aliquat 336	ClO_4^- , NO_3^- , Cl^-	142, 143
tetradodecylammonium	NO_3^-	144
hexadecylpyridinium	picrate	145
benzyl dimethylalkyl (C_8 - C_{18})	$\text{Co}(\text{SCN})_4^{2-}$	147
phenylethylammonium	chiral anions	146
Phosphonium, arsonium, oxonium salts		
tetradecylphosphonium	HgCl_3^- , TlCl_4^- , PF_6^-	148, 149
triphenylpyrylium	FeCl_4^-	150
tetraphenylarsonium	NbO_3^-	151
Basic dyes		
Victoria Blue	dodecylbenzene sulphate	152
Crystal Violet	NO_3^-	153
Methylene Blue	ClO_4^-	154
Cationic metal complexes		
Tris(4,7-diphenyl-1,10-phenanthroline)nickel(II)	NO_3^-	155
Tris(1,10-phenanthroline)ruthenium(II)	I^-	156
Ag-poly(thiourea-glutaraldehyde)cation	PO_4^{3-}	159
Uranyl-tributylphosphine oxide	NO_3^-	160
Bis(diethyldithiocarbamate)mercury(II)	SO_3^{2-}	162
Porphyrin and corrin derivatives		
5,10,15,20-tetraphenyl(porphyrinato)tin(IV) dichloride	salicylate	163
Cobalt(III) cobyrinate octadecyl cobester	NO_2^- , SCN^-	164
Cation exchangers		
Disubstituted phosphates		
Di-n-decyl phosphate	Ca^{2+}	165
Di-(4-octylphenyl) phosphate	Ca^{2+}	166
Di-4-(1,1,3,3-tetramethylbutyl)-phenyl phosphate	Ca^{2+}	167
Mono(2-ethylhexyl) phosphate	Ca^{2+}	168
β -Diketones		
Thenoyl trifluoroacetate	Ca^{2+}	169
Tetraaryl borates		
Tetraphenyl borate	Cs^+ , quaternary ammonium salts, alkaloids	170, 171
Tetra- <i>p</i> -chlorophenyl borate	K^+ , acetylcholine	172, 173
Thio derivatives		
Pyrrolidin-1-yl dithioformate	Cu^{2+}	174
O,O'-Didodecyldithiophosphate	Tl^+	175
Diphenylthiocarbazine	Cu^{2+} , Hg^{2+}	176
Thiourea	Au^+	177

Table 2. (contd)

Ion-carrier	Species sensed	Ref.
Various metal chelates		
Tris(2-nitroso-4-chlorophenyl) iron(III)	NH_4^+	178
Pyridylazonaphthol mercury	Hg^{2+}	179
<i>N</i> -benzyl- <i>N</i> -phenylhydroxylamine	Cu^{2+}	180
Various organic anions		
?,?-Dinonylnaphthalenesulphonate	polyvalent cations	181
2,4,6-Trioctyloxybenzenesulphonate	$\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$	182
Picrate	alkaloids	183
Dipicrylamine anion	alkaloids	184
Neutral ionophores		
Amines		
Tri- <i>n</i> -dodecylamine	H^+	185
Amides		
3-Hydroxy- <i>N</i> -dodecylpicolinamide	H^+	185
<i>N, N, N', N'</i> -tetraisobutylcyclohexane- - <i>cis</i> -1,2-dicarboxy amide	Li^+	186
1,1,1-tris-(5-methyl-4-oxo-2-oxa-5- azadecyl) propane	Na^+	187
(-)-(<i>R, R</i>)- <i>N, N'</i> -bis-[11-(ethoxycarbo- nyl)undecyl] <i>N, N'</i> -4,5-tetramethyl- 3,6-dioxaoctanediamide	Ca^{2+}	188
<i>N, N'</i> -dioctadecylmalonamide	Mg^{2+}	189
Organotin compounds		
Didodecyltin cation	phosphate and arsenate	157, 158
Trioctyltin cation	HCO_3^-	161
Depsipeptides		
Valinomycin	K^+	190, 191
Macrotetrolides		
Nonactin	NH_4^+	192
Non-cyclic polyethers		
Nigericin	Na^+	193
Monensin	Na^+	194
Thioamides		
<i>N, N, N', N'</i> -tetrabutyl-3,6-dioxa- octanebisthioamide	Cd^{2+}	195
Crown ethers		
Dibenzo-18-crown-6	K^+	197, 198
Bisbenzocrown-5-benzocrown-6	Rb^+	199
Cryptands		
1,4,8,11-Tetraazocyclotetradecane	$\text{Ni}^{2+}, \text{Ba}^{2+}$	200
Cryptand 222B	K^+	201
Cyclic thioethers		
3,4,7,8,10,11-hexahydro-6 <i>H</i> -2,5,9,12- benzotetrathiacyclopentadecin	Cu^{2+}	202
Polyethylene glycols		
Igepal CO 880	Ba^{2+}	203

In recent years OAR were also used for modification of electrodes for voltammetric techniques (204) to enable the determination of species which are inactive on non-modified electrodes as well as to improve the detection limits through the combination of enrichment on modified electrodes with stripping voltammetric procedures. The mechanism of the processes at the modified electrodes ranges from physical adsorption and extraction to formation of well defined compounds. Thus silanization with *N*-[(Trimethoxysilyl)ethyl]ethylenediamine or amidization with diethylenetriamine (205) makes possible the determination of the silver ions at extremely low concentrations enriched at the silanized or amidized carbon paste electrode (205). The hanging mercury drop electrode (HMDE) can be modified by dithizone for enrichment of copper (206), dithiooxamide acts in a similar way at a glassy carbon electrode (207). Tri-*n*-octyl-phosphine oxide permits enrichment of uranyl ions at the same support (208) or on a mercury electrode (209). Instead of tri-*n*-octylphosphine oxide also diisopropyl methyl phosphate may be used (210). The modification of a platinum electrode with poly(4-vinylpyridine) allows accumulation of chromium(VI) (211). Allylamine adsorbed at the platinum electrode makes possible the preconcentration of 10^{-7} mol/l ferrocenecarbaldehyde via definite chemical bonding (212). 3-Allylsalicylate chemisorbed on platinum via its olefinic group enables preconcentration of iron(III) (213). Bilayer electrodes may utilize the oxidizing or reducing capacity of the analyte. The consumption of trapped, viologen radical cation can be used to measure oxygen (214,215).

Recently a new group of OAR, namely biologically active substances, mainly enzymes (216) has given rise to biosensors. They can be used in solution or in immobilized form. It is outside the scope of this review to enumerate these in either of the two forms of application. However it must be mentioned that immobilization of enzymes has introduced into analytical chemistry a new group of OAR used for the immobilization reactions by formation of covalent bond. Important homobifunctional reagents are glutaraldehyde, biphenyl-4,4'-bisdiazonium-2,2'-disulphonate, bis-(4-fluoro-3-nitrophenyl) sulphone, 4,4'-dithiocyanato-biphenyl-4-hydroxybenzene-3-bis(sulphonyl chloride) and as heterobifunctional reagents 2-isocyanato-4-isothiocyanatotoluene, 2,4,6-trichloro-1,3,5-triazine, 3-methoxy-4,4'-diisocyanatodiphenylmethane. For immobilization of enzymes are often also required reagents which due to reaction with a carrier introduce a chemically active group (e.g., $-NH_2$ when 3-(triethoxysilyl)propylamine is used) on the carrier surface. The immobilized enzymes are used in construction of sensors based on potentiometric, amperometric or voltammetric principles, when the product of enzymatic reaction is electrochemically active.

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