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**APPLICATIONS OF ION-SELECTIVE
ELECTRODES IN NONAQUEOUS AND
MIXED SOLVENTS**

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1. Introduction
2. Problems of potentiometry in nonaqueous media
3. Potential response of ion-selective electrodes
 - 3.1. pH-sensitive glass electrodes
 - 3.2. Cation-sensitive glass electrodes
 - 3.3. Non-glass based ion-selective electrodes
4. Application of ion-selective electrodes in nonaqueous media
 - 4.1. Application of pH-sensitive glass electrodes
 - 4.2. Application of cation-sensitive glass electrodes
 - 4.3. Application of non-glass based ion-selective electrodes

1. INTRODUCTION

The processes taking place in nonaqueous, mixed and partially aqueous media are far more complex than those occurring in water. However, studies on the processes in these media with potentiometric technique employing different ion-selective electrodes opened up new possibilities for the further development in the field. Thus, determinations can be accomplished which are not feasible in aqueous media. At the same time the use of such solvent systems made possible a thorough examination of acid-base and complex equilibria, and of the mechanism and kinetics of different chemical reactions, as well as the investigation of ion-transport processes in solvent mixtures.

As it is known, in the interpretation of processes in nonaqueous media it is important to take into consideration the properties of the solvent (1-4) as will be described in Section 3.1. The application of ion-selective electrodes in nonaqueous solvents involves a series of problems in connection with the selection of the sensors and the measuring techniques. Among the ion-selective electrodes applied in nonaqueous and mixed solvents pH sensitive glass electrodes have found most extensive use. Consequently a series of questions regarding the mechanism of the operation of the electrodes in different non-aqueous solvents was investigated (e.g. pH-scales, liquid junction, potential response, etc.). The appearance of non-glass based ion-selective electrodes since the 1960's, offered new possibilities for the further development and widespread application of potentiometric techniques. Moreover their use in nonaqueous systems is expected.

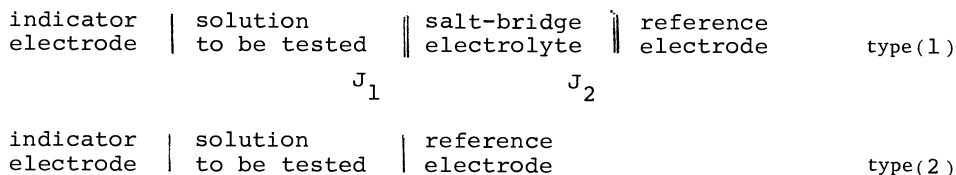
2. Problems of potentiometry in nonaqueous media

Sources of errors which are encountered in ion-selective electrode potentiometry in aqueous solutions have been reviewed, for example, by Durst (1,6-8). In the ion-selective electrode potentiometry in non-aqueous solvents, some additional problems other than those in aqueous solutions should be taken into account, as have been discussed by Pungor and Tóth (3). In the following a brief description will be given about problems and possibilities of the use of ion-selective sensors in non-aqueous, mixed and partially aqueous solvents.

Ion-selective electrodes: Ion-selective electrodes nowadays available have been prepared for use in aqueous solutions, and many of them are difficult to apply in non-aqueous solutions (not speaking about the pH-sensitive glass electrodes). Besides the problem of the proper response of the electrode, the materials constructing the electrode should not be damaged in the solvent under study. In general, it is true that the establishment of a well-defined phase boundary at the detector-solution interface is a condition of the use of an ion-selective electrode in nonaqueous solvents.

From the point of view of the application of potentiometric measuring techniques, the sensitivity, the Nernstian behaviour and selectivity of an indicator electrode is very important. From this point, glass electrodes and some solid membrane electrodes are promising. Ion-selective electrodes applicable in non-aqueous solvents and their conditioning will be described in Sections 3. and 4.

Cells, salt bridges, and reference electrodes: Two types of cells are usually employed for potentiometric study, i.e., cells with and without liquid junctions as shown by (1) and (2), respectively,



where | indicates a solution-electrode interface, and || a liquid junction. Cells of type (1) are usually used. In these cells, liquid junction potentials at J_1 and J_2 influence the emf of the cell. The liquid junction potentials should be reproducible and constant during a series of measurements. It is preferable that the solvent of the reference electrode is the same as that of the test solution. Moreover, if possible, it is recommended to eliminate the liquid junction potentials either (1) by adding an appropriate indifferent electrolyte to all solutions in the three compartments of cell, or (2) by using a high concentration of an equitransferent electrolyte solution in the salt bridge. It often occurs, however, that an aqueous electrode of the second kind (aqueous SCE, for example) is employed as the reference electrode. In those cases, big liquid junction potentials may be observed at the boundary between aqueous and non-aqueous (9) and the potential may be influenced significantly by the composition of the solutions at the boundary (10). The aqueous reference electrode should be connected to the test solution only through a salt bridge of appropriate non-aqueous solutions.

In cells of type (2), there is no liquid junction. However, this cell can be used only when the behaviour of the reference electrode in the test solution is exactly known.

The problem of the reference electrode is extremely important in potentiometry in non-aqueous solvents. Unfortunately no reference electrode in non-aqueous solvents is reliable enough in respect of stability and reproducibility of its potential. Detailed reviews (11-13) will be of help in choosing suitable reference electrodes.

Calibration of ion-selective electrodes: In general for the calibration of an ion-selective electrode other than the pH-sensitive glass electrode, a series of stable electrolyte solutions of different concentrations are prepared from well-defined, high purity salts. The effect of salt concentration on the activity coefficients of ionic species is often larger in non-aqueous solutions than in aqueous solutions, and the effect can be estimated by using an appropriate form of the Debye-Hückel equation. Correction should also be made for the effect of salt concentration on the liquid junction potential between the test solution and the salt bridge. The Henderson equation may be used for this. If there is no salt available which dissociates completely in the solvent under study, solutions of a salt of known dissociation equilibrium should be employed. In this case, of course, the calculation of ionic activities becomes more complicated. The purity of the solvent may also be very important. Small amounts of acidic and/or basic impurities, including residual water, may influence the calibration curve significantly.

3. Potential response of ion-selective electrodes

3.1. pH-sensitive glass electrodes

The fundamental principle of the operation of a pH-sensitive glass electrode is the interfacial potential difference between the hydrogen ions fixed in the membrane phase and solvated hydrogen ions in the solution

$$E_{1,(1)} = E_O + \frac{RT}{z_H + F} \ln \frac{a_{H,1}}{a_{H,(1)}} \quad (1)$$

where E is the phase-boundary potential,
 E_0 is a constant, l means the glass membrane phase,
 while (l) the solution phase, the other terms have their usual
 meaning

In practice the electrode process was found to be different from that described by equation (1). Boksay and Csákváry (14) have explained this fact in the following way: when an ion leaves the glass phase and enters the solution, a vacancy is produced in the glass surface. In the reverse process the ion entering the glass from the solution can occupy a vacancy only,



then the phase-boundary potential can be rewritten

$$E_{1,(1)} = E_0 + \frac{RT}{F} \ln \left[c_v \frac{a_{H,1}}{a_{H,(1)}} \right] \quad (3)$$

where c_v = the concentration of vacancies

Thus, the potential of the pH-sensitive glass electrode depends both on the activity of the hydrogen ion and the concentration of the vacancies.

In the case of a given type of glass and solvent, resp., the concentration of the vacancies can be regarded as constant provided that the rearrangement of the bond in the glass and the interfering effect of the molecules are excluded:

$$\text{thus} \quad E_{1,(1)} = \underbrace{E^0 + \frac{RT}{F} \ln c_v}_{E^0'} + \frac{RT}{F} \ln \frac{a_{H,1}}{a_{H,(1)}} \quad (4)$$

$c_v = \text{const.}$

However, in the course of the penetration of another solvent into the glass the concentration of the vacancies may change due to the change in the ion-exchange processes. So in the case of the measurements carried out in non-aqueous solvents, this fact must always be taken into consideration. This justifies and shows the importance of the conditioning, i.e. the preliminary soaking of the electrode in the given solvent.

The papers dealing with the problems related to the potential response of pH-sensitive glass electrodes have been summarized in Table 1. The main point of view discussed is the role of the internal reference solution and the effect of pretreatment of glass electrodes. There are different views regarding the selection of the internal filling solution (15-21).

The dynamic response of the commercially available glass electrodes was studied in detail by several authors (17,18,22-26) and it was found that the pre-conditioning of the glass electrode has shortened the time required for the establishment of a stable equilibrium potential. The acid error of glass electrodes in nonaqueous media was discussed also in some of the papers (27, 28).

The pH-sensitive glass electrode has been extensively used for thermodynamic studies in different media. In this context considerable effort has devoted to study the effect of non-aqueous solvents on acid-base equilibria. The extent of reactions in which protons are taking part depends on both electrostatic and chemical interactions. Changes in the nature of the solvents alter the position of equilibria of a protolytic reaction as well as the activity coefficient of ions. Due to this when ions are transferred from one solvent to another the so-called "transfer effect" can be observed. The transfer effect is a measure of the change in the free energy of transfer. Several papers have dealt with the correlation between of permittivity of the solvent and the transfer effect (29-37) mainly on the basis of the Børn theory. In work (1,32) there are detailed and critical surveys on these problems. On the basis of the above mentioned publications it can be stated that the Børn equation does not give a satisfactory explanation for the observed variations in the pK_a values. Certain attempts were made using methanol-water

mixtures (32) to get a linear correlation between the pK_a values of p-substituted phenols and the $1/\epsilon$ of the corresponding solvent media on the one hand, and between the Hammett's σ_s and $1/\epsilon$ on the other. However, the expected linearity predicted on the basis of the simple Born equation was not observed in any of the cases studied. These results gave also a confirmation of the limited applicability of the simple electrostatic treatment to the transfer problems of ions.

In paper (33) a study is given dealing with the behaviour of a series of organic acids in nonaqueous media. Three different binary solvent systems were employed each extending over the range of $\epsilon = 5-30$. The solvents were chemically inert, nonleveling and nonreactive (benzene-nitrobenzene, benzene-nitromethane and benzene-acetone systems). The slopes of the HNP vs. pK_a curves plotted against the dielectric constants of different solvent systems result different curves depending on the nature of the solvent system, indicating that the permittivity on its own is not sufficient to describe the phenomena.

In other papers (31,33,38-41) there are also data on the relationship between pK_a or pK_b values obtained in pure water and the half neutralization potentials (HNP) in potentiometric titrations of acids and bases in different nonaqueous media. To eliminate the shifts caused by electrostatic effects, liquid junction potentials, etc. it was expedient to use a reference standard, so to calculate instead of HNP of each acid or base with the differential half neutralization potential (HNP)(40). In other cases good results were obtained by extrapolating the data to zero dielectric constant (33).

Korolev (42) studied the dissociation constants of NH- and OH-type organic acids in water and various organic solvents. Other authors examined amines in nitromethane (43) NaCl in nitromethane (35), organic acids in propylene carbonate (44), alkali metal chlorides (45) and HCl (46) in dimethyl sulfoxide-water mixtures (45), chloride ion in tert-butanol (47), HCl in N-methylacetamide-water mixtures (48), NaCl in aqueous glycerol solutions (49). These publications have dealt with the problem of solvation of ions in different organic solvents and in mixed solvents. The papers on the effect of solvents are summarized in Table 2.

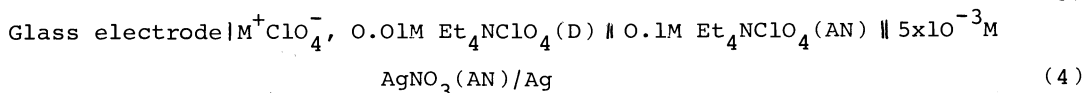
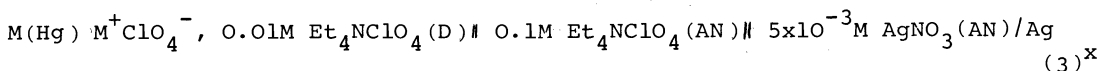
3.2. Cation-sensitive glass electrodes

Nernstian response: Many investigators have confirmed the Nernstian response of cation-sensitive glass electrodes in different aqueous and nonaqueous solvent mixtures. Eisenman (50) showed that the glass electrode may be used to measure the activities of alkali metal ions in methanol (MeOH). McClure and Reddy (51) reported that a cation-sensitive glass electrode (Beckman, 39047) responds in a nearly Nernstian way to K^+ , Na^+ and Li^+ in acetonitrile (AN) and propylene carbonate (PC) and to K^+ in dimethylformide (DMF) in the concentration range between 10^{-5} and $10^{-2}M$ in the presence of $0.1M Bu_4NClO_4$ as an indifferent electrolyte. The response for Na^+ and Li^+ in DMF, however, was unsatisfactory. Each electrode was in contact with only one kind of solvent throughout the work: the electrode stored in PC ($10^{-2}M Li^+$) showed no sign of deterioration even after six months, but the electrode stored in AN became pitted and ceased to respond after three months. The response of the electrodes was rapid, and an equilibrium potential within 1 mV was attained in 5 to 10 s. Chantooni and Kolthoff (52) used the same kind of electrode (Beckman, 39047) to determine the activities of K^+ in AN, DMF, and dimethyl sulfoxide (DMSO) and Na^+ in AN and DMSO. (Na^+ in DMSO gave a Nernstian response only above $10^{-2}M$.) About 10 min was required to get stable potentials reproducible within ± 2 mV. The same electrode was also confirmed to respond to Rb^+ , Tl^+ and NH_4^+ in AN with a Nernstian slope, but the slope for Cs^+ in AN was ca. 43 mV (53).

Mukherjee and Boden (54) studied the response characteristics of a glass electrode (Beckman, 39137) in solutions of pure Li^+ salt in PC and in the presence of such cations as K^+ , NH_4^+ and Et_4H^+ at a concentration of $0.25M$. Only Et_4N^+ did not interfere with the response of the electrode to Li^+ . Kolthoff and Chantooni (55) calibrated K^+ -electrode (Markson Co., 1002) for K^+ and Tl^+ and Na^+ -electrode (Markson Co., 1001) for Na^+ in MeOH, AN, PC and DMSO. The electrodes were conditioned for 3-4 days in a $0.01M$ solution of the perchlorate or picrate salt in the same solvent in which $pa(M^+)$ was measured. The slopes of the calibration curves for perchlorates of Na^+ , K^+ and Tl^+ (for the concentration ranges of ca. 10^{-4} - $5 \times 10^{-3}M$) in AN, PC, DMSO and MeOH were almost Nernstian ($59.1 + 0.5$ mV/pa(M^+) at $25^\circ C$), except for K^+ in DMSO (63.8 mV) and Tl^+ in PC (54 mV). Stable potentials to within ± 1 mV were obtained in 5 min, except in PC which required 10-20 min.

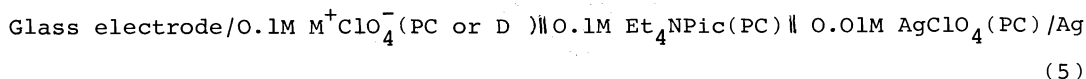
Comparison of activities in different solvents: Eisenman (50) compared the potentials of a cation-sensitive glass electrode (NAS 11-18) vs. Ag/AgCl reference electrode in saturated solutions of NaCl in pure H₂O, pure MeOH, and mixtures of H₂O and MeOH. The potential values were the same within a fraction of a millivolt, showing that there was no special solvent effect on the surface of the glass electrode and that the electrode can be used to compare ionic activities in those solvents. For (NAS 27-3 + 3ZnO) glass electrode, however, the potentials in H₂O and MeOH differed by 15-20 mV, indicating the existence of some solvent effect on the surface properties. Cells with a cation-sensitive glass electrode and an Ag/AgCl reference electrode (type (2)) have been used to obtain free energies of transfer of alkali metal chlorides from water to various aqueous organic solvents (56-61). Covington and Thain (62) determined free energies of transfer of alkali metal fluorides and chlorides from water to aqueous MeOH by using cation-sensitive glass electrodes and as a reference electrode an F-selective electrode (Orion, 94-09) for fluorides and a Cl⁻-selective electrode (Orion, 94-17) for chlorides. They compared several glass electrodes (Orion Na⁺, 94-11A; E.I.L. Na⁺, GEA 3313 or 33-1048-100; Corning univalent cation, 476200; and E.I.L. K⁺, 33-1057-200) as to the specific solvent effect on the electrode potentials.

Nakamura (63) studied the response of a cation-sensitive glass electrode (Beckman, 39047) to the activities of various univalent cations in different solvents. He compared emfs of cells (3) and (4),



where D is AN, PC, MeOH, H₂O, DMF or DMSO, and M⁺ is Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Tl⁺ or Ag⁺. (*Ag wire was used instead of Ag amalgam for M⁺ = Ag⁺.) The results are shown in Fig.1, choosing AN as a reference solvent (Fig.1.). It is apparent that, in many cases, the glass electrode behaved in the same way as the corresponding amalgam electrodes. There are some exceptions, however, in which deviations occurred. Ag⁺ in AN deviated significantly, and some cations in H₂O also deviated to a smaller extent.

Cox et al. (64,65) obtained free energies of transfer of Li⁺ and Na⁺ from PC to DMA, DMSO, and DMA-PC, DMSO-PC mixtures by measuring emfs of cell (5),



where the glass electrode is Corning univalent cation-sensitive electrode and D shown solvents to which M⁺ is transferred. The liquid junction potential at J was considered to be negligible (66). Free energies of transfer for Na⁺ were also obtained using an amalgam electrode, fair agreements being obtained between both results. They also calculated the free energies of transfer of these cations from the successive formation constants of complexing of these ions in PC with DMA and DMSO, by assuming that interaction energies outside the first coordination sphere were independent of the solvent species. The values provided by calculations agreed well with the experimental values obtained with cell (5).

From these results it is apparent that the cation-sensitive glass electrodes can be applied to compare ionic activities in different solvents. But it is necessary to confirm beforehand, by some appropriate methods, that the potentials of the electrode to be used are not affected specifically by the solvents in question.

Note on the selectivities of cation-sensitive glass electrodes. Some results have been reported on the selectivities of cation-sensitive glass electrodes in non-aqueous solvents (50,51,67,68), but no systematic investigation has been carried out. When the glass electrode can respond in a Nernstian way to the activities of univalent cations in different solvents, the solvent effect to the selectivity constants of the electrode is considered to be determined mainly by the changes of solvation energies of the cations.

3.3. Non-glass based ion-selective electrodes

As it was proved by a number of scientists, similar calibration curves can be obtained in general for different ion-selective electrodes in nonaqueous and

in mixed media as in aqueous solutions.

Many authors examined (69,70,71,72,73,74,75,76,77,78,80-86) the potential response of silver iodide electrodes as well as that of silver bromide electrodes (72-74, 78) in detail. Publications on silver chloride ion selective electrodes (72-74, 87-90) deal with certain theoretical problems important in respect of applications in nonaqueous media. In connection with fluoride ion-selective electrode there are numerous publications (87,91-96) but only a few papers deal with the potential response of copper (97-99) and lead ion-selective electrodes (100-104). The data published in the papers already mentioned are summarized in Table 3. according to the solvents applied. The application conditions are discussed in detail in Section 4.3.

There are publications reporting on electrodes containing new electrode active materials, which are summarized in Table 4. On the basis of the above literature data it can be stated that the investigation of potential response, dynamic properties, selectivity, etc. of non-glass based ion-selective electrodes requires further research work in the future not only from practical but also from theoretical points of view.

4. Application of ion-selective electrodes in nonaqueous media

Although most of the applications of ion-selective electrodes are limited to aqueous solutions, the number of examples of successful applications in non-aqueous solutions is increasing steadily. The present report will review these applications of ion-selective electrodes in non-aqueous solutions.

Ion-sensitive electrodes in organic solvents have been used as:

- (i) an indicator electrode for physicochemical studies, including those on ion association and complexation of univalent cations
- (ii) an indicator electrode for analytical titrations of univalent cations and of reagents which can complex univalent cations (macro-cyclic polyethers, for example),
- (iii) a reference electrode in the solutions containing univalent cations.

4.1. Application of pH-sensitive glass electrodes

The majority of papers are dealing with determination of analytical concentration values of organic acids and bases. At the same time, from the potentiometric data first of all thermodynamic constants, e.g. stability constants of complexes containing organic ligands, acid-base equilibrium constants of organic compounds, etc. are determined. These papers are summarized in Tables 5-10.

4.2. Application of cation-sensitive glass electrodes

The cation-sensitive glass electrodes are very convenient for the study of complexing of univalent cations. Frensdorff (105) used Na^+ -selective electrode (Corning NAS 11-18, 476210) and univalent cation-sensitive electrode (Corning, 476220) for Na^+ and Li^+ , K^+ , Cs^+ and NH_4^+ , respectively, to study the complex formation constants of these cations in MeOH with macrocyclic polyethers. (The cation electrode was conditioned for each new cation by soaking it overnight in a 0.01-0.1M solution of its chloride. One such electrode cracked on immersion in MeOH, but other electrodes were successfully used in MeOH by stepwise conditioning in aqueous solution of increasing MeOH content up to pure MeOH, in which they could be kept indefinitely.) Kolthoff and Chantooni (55) studied complex formation constants of Na^+ , K^+ , Rb^+ , Cs^+ and Tl^+ in AN, PC and DMSO with various macrocyclic polyethers. Izutsu et al. (106) determined complex formation constants of Na^+ in AN with several macrocyclic polyethers at 10, 25, and 40°C and obtained thermodynamic parameters (ΔG° , ΔH° and ΔS°) for the 1:1 complexing processes. In such protophobic solvents as AN and PC, alkali metal ions form stable 1:1 complexes with macrocyclic polyethers. Thus, the glass electrodes are convenient for potentiometric titrations of alkali metal ions with polyethers and vice versa.

Izutsu et al. (53,107,108) and Nakamura (109,110) used a glass electrode (Beckman, 39047) to study the complexing of univalent cations in AN with other solvent molecules, and obtained successive formation constants of Li^+ , Na^+ , K^+ , Rb^+ , Tl^+ and NH_4^+ with such solvents as MeOH, dimethylacetamide (DMA) (DMF), dimethylthioformamide, DMSO, pyridine and hexamethylphosphoric triamide (HMPA). Izutsu et al. (106) also used the electrode to obtain thermo-

dynamic parameters for the complexing of Li^+ in AN with DMF, DMA, DMSO and HMPA. Cox et al. (111,112) also determined by a similar method the successive formation constants of Na^+ and Li^+ in PC with DMA and DMSO. They found species complexed up to four solvent molecules per ion.

Pataki et al. (79-86) determined the mean activity coefficients of Na^+ and I^- ions in MeOH, ethanol, n-propanol, n-butanol, n-pentanol, n-heptanol, and n-octanol solutions of NaI by measuring emfs of liquid junction-free cells (cells of type (2)) equipped with a Na^+ -selective electrode (Radelkis OP-Na-711-D) and an I^- -selective electrode (Radelkis OP-I-711-D).

Cation-sensitive glass electrodes can also work in liquid ammonia of ca. -33°C . Shiurba and Jolly (113) measured the activity of NH_4^+ in liquid ammonia by using a cation-sensitive glass electrode (Beckman, 39137; but with internal solution of aqueous 8M HCl saturated with AgCl) and a Ag/Ag⁺ reference electrode. They got a response of 50 mV/pNH₄⁺ (theory: 48 mV). Titrations of potassium amide, potassium hydroxide, and their mixture with ammonium bromide gave sharp inflection point(s). Baumann and Simon (114) obtained a slope of 47 mV for NH_4^+ in liquid ammonia by using an NH_3 -saturated Cd-Cd(NO₃)₂ reference electrode. They also used the electrode for the titration of potassium salts of very weak acids in ammonia.

Notz and Keenan (67) and Wilcox (115) studied in fused ammonium nitrate at 190°C the response of a Pyrex bulb electrode to the contents of nitrate salts of various univalent cations and several divalent cations. A fritted Ag/Ag half-cell was used as a reference electrode. The Pyrex electrode behaved in a way as expected from the ion-exchange model which had been developed for the glass electrode in aqueous solutions. The papers are summarized in Table 11.

4.3. Application of non-glass based ion-selective electrodes

Chloride, Bromide, and Iodide-Selective Electrodes:

Heterogeneous electrodes. Kazaryan and Pungor (69-75) studied the behaviour of silicone-rubber based halide ion-selective electrodes in aqueous organic solvents containing alcohols, acetone, DMF, etc. Aqueous SCE with KNO₃ salt bridge was used as a reference electrode. The electrodes could function satisfactorily, without any damage, in solvents containing up to 90 v/v % of MeOH or ethanol, 40% of propanol or isopropanol, and 60% of acetone or DMF. Above these limits, however, the electrodes did not function satisfactorily: the silicone rubber matrix swelled continuously and, at the same time, the color or the solvent mixture changed. The color change was attributed to the dissolution of the precipitate in colloidal form. Benzene-MeOH mixture was also tested as a solvent, but the mixture made the silicone rubber membrane fragile. Kazaryan and Pungor also tested the relation between lower limit of response of the electrode and the solubility of the precipitate of silver halides. In solutions containing 90% of MeOH, the lower detection limit of the I^- -selective electrode was at 10^{-9} M I^- as expected from the small solubility of AgI. But in such mixed solvents the selectivities of the electrodes were poorer than in H₂O.

The behaviour of SCN^- -selective silicone-rubber membrane electrode (Radelkis OP-SCN-712-C) was studied in aqueous organic solvents containing 20-80% of ethanol, acetone, DMF, DMSO, and 1,4-dioxane (116). An increase in the concentration of the organic solvent increased the sensitivity of the electrode but decreased its selectivity.

Homogeneous electrodes. Ficklin and Gotschall (78) used homogeneous solid Br^- and I^- -selective electrodes and obtained calibration curves for Br^- in MeOH, ethanol, butanol, pentanol, hexanol and acetic acid and for I^- in MeOH and ethanol. The electrode for Br^- was Orion 94-35 and that for I^- was Orion 94-53. In all solvents tested, the electrodes worked with near-Nernstian slopes. Kazaryan et al. (76) studied the behaviour of I^- -selective electrode in alcohols and aqueous alcohols (MeOH, ethanol, propanol, isopropanol, butanol, isobutanol, isoamyl- and n-hexylalcohols) and got linear responses for 10^{-6} - 10^{-1} M I^- . They developed direct potentiometric and potentiometric titration methods for the determination of halides with the electrode.

Iodide-selective electrodes (Radelkis OP-I-711-D) have been used to determine the mean activity coefficients of Na^+ and I^- in various alcohols (79-86). When the concentration of I^- was larger than 10^{-2} M, the electrode behaviour deviated from the reversible one due to the complex formation of I^- with AgI electrode.

Kazaryan et al. (90,117) investigated the behaviour of homogeneous Cl^- -selective electrode in non-aqueous MeOH, ethanol, propanol, isopropanol, acetone and DMF, and in their 10-90% mixtures with H_2O . The slopes of the calibration curves, obtained in solutions of Et_4NCl , were 35-40 mV/pCl for pure organic solvents and 38-50 mV/pCl for mixed solvents. The lower detection limit for Cl^- was 10^{-6}M in pure MeOH, ethanol and DMF, 10^{-7}M in propanol, and 10^{-8}M in isopropanol and acetone. A Cl^- -selective electrode was used in AN titrate Cl^- in the presence of Br^- with Ag^+ after the selective oxidation of Br^- with KMnO_4 or $\text{Ce}(\text{SO}_4)_2$ (88).

Izutsu et al. (118) used ceramic halide-selective electrodes ($\text{Ag}_2\text{S} \cdot \text{AgX}$) in MeOH, ethanol and PC. Test solutions of ($\text{Et}_4\text{X} + 0.01\text{M Et}_4\text{NClO}_4$) were connected to the reference electrode ($\text{Ag}/0.005\text{M AgClO}_4, 0.01\text{M Et}_4\text{NClO}_4$) through a salt bridge of $0.05\text{M Et}_4\text{NClO}_4$. The Cl^- -selective electrode (Matsushita, IE-560103) gave Nernstian slopes to 2×10^{-5} - 10^{-1}M Cl^- in all solvents tested, but the dissolution of the electrode surface was considerable in PC containing high concentrations of Cl^- . The response of Br^- -selective electrode (Matsushita, IE-560104) to Br^- was Nernstian in MeOH and ethanol, but super-Nernstian (95 ± 1 mV/pBr for 10^{-5} - 10^{-1}M Br^-) in PC. The electrode surface was also etched in PC. The response of I^- -selective electrode (Matsushita, IE-560105) to I^- was super-Nernstian in all solvents tested (83 mV in MeOH, 93 mV in ethanol and 68 mV in PC). All these electrodes responded in a Nernstian way to Ag^+ in all solvents. They attributed the super-Nernstian responses of the ceramic electrodes to the slow rates of dissolution of the electrode materials ($\text{Ag}_2\text{S} \cdot \text{AgX}$).

Homogeneous halide-selective electrodes can be used as indicator electrodes in anhydrous alcohols, but their responses are not always Nernstian. Thus, for physicochemical uses, the potential response of the electrode should be tested beforehand. In aprotic solvents containing high concentrations of halide ions, slow dissolution of electrode materials occurs because the halide ions form stable complex ions $[\text{AgX}_2]^-$ with AgX of the electrodes. Although Nernstian responses are sometimes obtained in aprotic solvents, the electrodes are not durable for long time in those solvents.

Fluoride Ion-Selective Electrodes:

Single Crystal lanthanum fluoride electrodes for F^- ion can be used in organic and aqueous organic solvents which do not damage the electrode and the electrode body. Among those organic solvents are MeOH, ethanol, acetone, AN and PC, and even DMSO has been reported to be a such solvent (93).

Lingane (91,92) showed that the response of an F^- -selective electrode (Orion product) to F^- in 60% aqueous ethanol was Nernstian and that the addition of 60-70% ethanol was very effective to improve the potentiometric titration curves of F^- with Th^{4+} , La^{3+} and Ca^{2+} . Heckel and Marsh (119) could titrate, using an F^- -electrode (Orion 96-09), subnanomole quantities of F^- in 2 ml solutions in polar solvents (MeOH, ethanol, propanol, acetone and 1,4-dioxane) containing 5% of water with La^{3+} . F^- -selective electrodes are often used in aqueous organic solvents in titrations of F^- with metal ions and of metal ions with F^- . Zhukov et al. (120) used the electrode to titrate SO_4^{2-} with Ba^{2+} in 40-90% acetone or ethanol containing a known amount of NaF.

Bixler and Bond (121) investigated the behaviour of an F^- -electrode (Orion 94-09A) in MeOH and applied it to study the stabilities of alkaline earth monofluoride complexes $[\text{MF}]$ in MeOH and aqueous MeOH. Coetzee and Martin (96) recently investigated, by direct potentiometry and potentiometric titrations, the response of an F^- -electrode (Orion 94-09) in a variety of alcohols and dipolar aprotic solvents and their mixtures with water. In direct potentiometry, the electrode was calibrated in Et_4NF containing $0.01\text{M Et}_4\text{NClO}_4$ or Bu_4NClO_4 . The reference electrode, a modified-SCE in alcohols and $\text{Ag}/0.01\text{M AgClO}_4$ (AN) in other solvents, was used with a salt bridge of $0.1\text{M Et}_4\text{NClO}_4$ in the pertinent solvent. To obtain stable potentials ca. 10 min was required. The slopes of the calibration curves and the lower limits of detection are shown in Table 13. The response in anhydrous solvents was somewhat super-Nernstian, especially for F^- activities in 10^{-5} - 10^{-6}M range. The response became almost Nernstian when some water was added. The response of the F^- -electrode was more ideal in potentiometric titrations of F^- with metal ions. Coetzee and Martin applied the titration method to determine solubility product constants of LaF_3 in various solvents and of NaF , NiF_2 and MnF_2 in AN. They also showed that the addition of organic solvents to aqueous samples could improve the sensitivity of direct potentiometry by up to 1 decade, and that of potentiometric titration by 2-3 decades.

Menard et al. (122) used a LaF_3 electrode to measure F^- activities in anhydrous HF and HF- H_2O mixtures. Because of the strong corroding action of anhydrous HF, the use of a commercial electrode was impossible. They built an HF-resistant electrode with a Teflon sleeve.

Solid-State Heavy Metal Ion-Selective Electrodes:

Various organic solvents are often added to aqueous solutions to improve the results of potentiometric titrations with solid-state heavy metal ion-selective electrodes. In the analyses of inorganic sulfate (123), organic sulfur (124,125) and oxalate (126), for example, aqueous 1,4-dioxane was used as a solvent to titrate with Pb^{2+} using a Pb^{2+} -selective electrode. The behaviour of Pb^{2+} -selective electrode (Orion 94-82 A) in various organic solvents was studied recently (103,104).

Solid-state heavy metal ion-selective electrodes can also be used in anhydrous organic solvents. Rechnitz and his coworkers studied the use of a Cd^{2+} -selective electrode in the titration of $\text{Cd}(\text{NO}_3)_2$ in DMSO with EDTA (127), and of a Cu^{2+} -selective electrode in the titration of $\text{Cu}(\text{ClO}_4)_2$ in MeOH, acetone and AN with EDTA, tetraethylenepentamine and 5,6-dimethyl-1,10-phenanthroline (97). Heerman and Rechnitz (128) used a cuprous sulfide-membrane electrode for the potentiometric measurements of Cu(I) in AN containing 0.1M Et_4NClO_4 or NaClO_4 as an indifferent electrolyte. The electrode showed near-Nernstian response (55-56 mV/decade) for Cu(I) down to 10^{-5} M in pure solutions and at least 3×10^{-7} M in the presence of complexing ligands. The electrode was used to measure successive formation constants of Cu(I) complexes with halide ions and thiourea in AN. Recently, Coetzee and Istone (99) studied the response of a Cu(II) ion-selective electrode having a composition of $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ in solutions of Cu(II) in various alcohols and aprotic solvents and their mixtures with water. In all solvents, except AN, the slope in the linear region was Nernstian or slightly sub-Nernstian and the lower limit of the linear region was at 4-5 pCu. They used the electrode to estimate free energies of transfer of Cu(II) between different solvents and solvent mixtures. Coetzee et al. (98) studied the reason why the electrode did not work correctly in AN and showed by ESCA and other studies that, in solutions of certain Cu(II) salts in AN, the electrode failed because Cu(II) replaced Cu(I) and Ag(I) ion was leached from the electrode.

In Tables 12-19 the trends of application of non-glass based ion-selective electrodes in non-aqueous media are summarised.

On this basis it can be stated that the application of ion-selective electrodes in non-aqueous and mixed solvent is continuously gaining ground, while in contrast, the properties and response mechanism of these electrodes in the various media are not sufficiently known yet, so that further research activity is required in this area in the future.

Moreover, it can also be concluded that the needs for analytical and physico-chemical applications of ion-selective electrodes in non-aqueous solvents are now increasing rapidly, and the development of new ion-selective electrodes which can be used for other ions in non-aqueous solvents is highly desired.

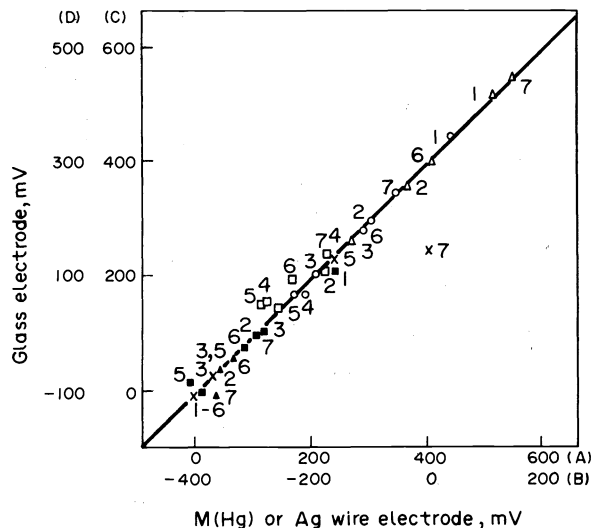


Fig. 1. Comparison of emfs of cells 3 & 4

A & B for cell 3; C & D for cell 4

A & C show emf D emf D = AN for M other than Ag

B shows emf D emf D = AN for M = Ag

D shows emf D for M = Ag

M: 1 Li, 2 Na, 3 K, 4 Rb, 5 Cs, 6 Tl & 7 Ag

D: O AN, PC, H_2O , DMF, and DMSO.

Table 1. Potential response of glass electrodes

SOLVENT	Studies made	Ref.
iso-PrOH, methyl ethylketon, and its biner systems	Stability of a glass Ag/AgCl cell was investigated	22
liq. ammonia	The electrode responds to NH_4^+ ion	129
water-MeOH DMF-water	The effect of the composition of inner solution was studied	17,18
MeOH, DMF, AN	The role of the conditioning of the electrode in the appropriate solvent (dehydration of the gel layer)	24
iso-PrOH	The cause of the slow response was investigated (dehydration of the glass surface)	25
sulfolane	Comparison of glass and hydrogen electrode	130
30% aqueous DMSO	The cell functioned normally at 25 and -12°C	131
aliphatic alcohols, ketones and their biner systems with water	The acid error of pH-glass electrodes was investigated in concentrated aqueous acids and in organic solvents	132

Table 2. Effect of solvents

SOLVENTS	Subject	Ref.
dipolar aprotic solvents	classification of org. solvents, acid-base equilibria, effect of hydrogen-bond, titrn. of very weak bases and acids, effect of dielectric constant, etc.	2
biner systems (water-dipolar aprotic solvents)	effect of the dielectric properties of mixed solvents on the liquid junction and the H^+ ion, resp.	29
water-n-PrOH	Dissociation constants of some ligands and formation constants of metal chelates in a dielectric constant range of 30-80	30
benzene-AN	titration and pK_a values of numerous acids and bases in mixed systems with dielectric constants in the range of 5-35	31
benzene-AN, benzene-nitrobenzene, benzene-nitro-methane, benzene-acetone	Relationships between the pK_a of acids and their half neutralization point, effect of the ϵ of solvent systems	33
pyridine	titration of some organic acids, effect of solvent on their half neutralization point	39

cont. Table 2.

SOLVENTS	Subject	Ref.
AN, pyridine, 4-methyl-2-pentanone, 2-nitropropane, o-nitrotoluene, nitrobenzene, DMF, chlorobenzene, bromobenzene	titration of substituted aromatic acids, relationship of half neutralization point with pK_a and Hammett's σ	40
glacial acetic acid, acetone, AN, iso-PrOH, nitromethane	relationship is given between $pK_b(H_2O)$ of some organic bases and their half neutralization points	41
dioxane-water	titration of some sulpha-drugs in biner solvent systems, correlation of mole fraction of dioxane and pK values	36
iso-PrOH, tert.-butanol	titration of dibasic organic acids, effect of the ϵ	133
methanol-nitromethane	Changing in solvation of NaCl and activity coefficients in organic systems in the range of $\epsilon = 32, 1-81$	35
nitromethane	Change of solvation of substituted ammonium ions on the basis of the slope of the correlation between pK_a values and Taft constants	43
nitromethane, AN, DMSO	Solvation of ions and effect of substituents on the acidity of NH^- and OH^- acids	42
methanol-water	Solvation of some 4-substituted phenols, the validity of the Born equation and the Hammett function in biner systems	32
iso-PrOH, tert.-butanol, n-hexanol	Acid-base equilibria, solvation constant of chloride ion in tert.-butanol	47
water-glycerol	solvation of NaCl in biner systems, activity coefficients, data in comparison with those obtained in ethylene glycol	49
MeOH-nitromethane	Solvation of NaCl, the trend of change in solvation and activity coefficients, resp. with the composition of solvent system	35
DMSO-water	Solvation and activity coefficients of HCl and changing with the dimethyl sulphoxide content of the solvent	46
water-dioxane	Protonation constants of glycine and stability constants of their metal complexes in function of solvent composition	134
AN-water, MeOH-water, dioxane-water	Acid-base equilibria, protonligand stability constants in various solvent systems	135
tert.-butanol, pyridine, acetone, iso-PrOH	The effect of the solvents on the electrode potential of the glass electrode is discussed	329
AN	The calibration of the glass electrode in AN was investigated in detail	330

Table 3. Potential response of non-glass based ion-selective electrodes

ELECTRODE	Subject, Media	Ref.
silver iodide, silicone rubber based	Potential response in methanol, ethanol, propanol, isopropanol and their mixtures with water	69
	Potential response and swelling in aqueous mixtures of methanol, ethanol, benzene, acetonitrile and dimethyl formamide	70
	Detection limit and solubility products in methanol, ethanol, propanol, isopropanol, dimethyl formamide, methanol-benzene mixtures	71
	Applicability in mixtures with water of acetone and dimethyl formamide	72
	Determination of solubility product values in aliphatic alcohols, acetone and dimethyl formamide	73,74
	Potential response and applicability in pure nonaqueous solvents	75
silver iodide	Potential response and detection limit in aqueous aliphatic alcohols	76
	Determination of solubility product values in aqueous aliphatic alcohols	77
	The effect of organic solvent content of medium on the potential response	78
	Determination of the mean activity coefficient values in pure nonaqueous solvents as follows: EtOH, n-PrOH, MeOH, n-BuOH, n-heptanol, n-octanol	79,80,81,82,83,84,85,86
silver bromide, silicone rubber based	Applicability in aqueous mixtures of acetone and DMF	72
	Determination of solubility product values in aliphatic alcohols, acetone and DMF	73,74
	The effect of organic solvent content of medium on the potential response	78
silver chloride, silicone rubber based	Applicability in aqueous mixtures of acetone and DMF	72
	Determination of solubility product values in aliphatic alcohols, acetone and DMF	73,74
silver chloride	Determination of free energy of transfer of alkali chlorides in methanol + water mixtures	87
	Applicability in AN	88
	Potential response and detection limit in isopropanol and in its mixtures with water	89
	Potential response and other properties in MeOH, EtOH, PrOH, iso-PrOH, acetone and DMF	90
lanthanum fluoride, single crystal	Determination of free energy of transfer of alkali fluorides in methanol + water mixtures	87

cont. Table 3.

ELECTRODE	Subject, Media	Ref.
	The role of organic solvent content on applicability of the electrode in aqueous ethanol	91
	Properties of the electrode in aqueous ethanol	92
	Applicability in DMSO	93
	Potential response and detection limit in aqueous MeOH, EtOH, PrOH, acetone and dioxane	136
	Potential response in MeOH	95
	Potential response and other properties in alcohols, dipolar aprotic solvents and their mixtures with water	96
lanthanum fluoride, polycrystalline	Properties in aqueous MeOH, EtOH, acetone and dioxane	94
copper	Applicability in MeOH, acetone and AN	97
	Potential response studies in connection with the change of the electrode surface in AN	98
	Determination of free energy of transfer of copper ion in water-propanol, isopropanol, ethylene glycol and sulfolane mixtures	99
lead	Applicability in MeOH, DMSO, 1,4-dioxane and AN	100
	Preparation and applicability in aqueous acetone	101
	Applicability in dioxane	102
	Effect of permittivity on the electrode in aqueous mixtures of MeOH, EtOH, acetone, DMSO and dioxane	103
	Potential response in aqueous MeOH, EtOH, PrOH, ethylene glycol and glycerol	104

Table 4. Ion-selective electrodes based on different electroactive materials

Ion, for	ELECTRODE, MEDIA	Ref.
chloride	Ion-exchange type, in amylalcohol	137
anions	ion-exchange type, in aqueous MeOH, EtOH and PrOH	138
bivalent cations	ion-exchange type in aqueous PrOH	139
H ⁺ and Cl ⁻	ion-exchange type in pure EtOH	140
4,7-DPP anion	Silver complex of 4,7-diphenylphenantroline (4,7-DPP), in aqueous EtOH and acetone	141
SCN ⁻	AgSCN electrode, in different aqueous mixtures of EtOH, acetone, DMF, dioxane and DMSO	116
picrate	picrate salt of crystal violet, in a two-phase system of nitrobenzene, toluene or chloroform with water	142
phenolate anions	phenolate salt of crystal violet, in two-phase system of nitrobenzene and water	143

cont. Table 4.

Ion, for	ELECTRODE, MEDIA	Ref.
sulfide	As ₂ S ₃ , arsenous sulfide, in alcohols	144
anions of C ₉ -C ₁₈ aliphatic acids	Pelargonate salt of crystal violet in two-phase systems	145
picrate	Picrate salt of crystal violet in two-phase systems	146
R ₄ N ⁺ cations	Tetrabutylammonium tetraphenylborate in PVC in aqueous EtOH	147

Table 5. Stability constants of metal chelates

SOLVENT	SUBJECT	Ref.
aqueous n-PrOH	Metal chelate stabilities of Ni(II) and Zn(II) complexes of picolin. and pipercolinic acids	30
DMF	Study on the stability of Ni complexes of dialkyl-148 dithiocarbamates. Stability constants data are given	
aqueous MeOH, EtOH, acetone	A critical survey of hydroxo complexes of Be	149
3:1 dioxane-water	Stability data of Ni, Zn, Cd, Hg(II), Pb(II) and UO ₂ (II) complexes of some monothio-β-ketones were determined	150
50% aqueous dioxane	Stability constants of binary complexes of lanthanides with thiotropolone	151
aqueous dioxane	Study on equilibrium constants of UO ₂ (II)-malonic acid complexes	152
60% aqueous MeOH	Stability constants of some Schiff base complexes with Cs, Ag, Zn, Cd, Hg(II) and Co are given and discussed	153
50% aqueous dioxane	Potentiometric study of the complexes of In(III) with some azo dyes. Stability data are given	154
75% aqueous dioxane	Formation constants of Cu, Ni, Co and Zn chelates of 2-hydroxy-1-naphthalidene-2',5'-dimethoxyaniline	155
aqueous DMF	Formation constants of vanadyl complexes of benzoyl- and nicotinyl hydrazines	156
50% aqueous acetone	Stability constants of 2-mercaptomethylbenzylimidazole complexes with Zn, Co and Ni are reported	157
60% aqueous dioxane	Formation constants of 2-hydroxy-5-methylbenzophenoneanil with Cu, Zn, Cd, Ni, Co, Mn are given and discussed	158
0-64% aqueous EtOH	Stability of complexes of Ni with monoethanolamine is discussed	159
10-70% aqueous dioxane	Potentiometric study on Cu and Zn complexes of glycine	134
40-60% aqueous dioxane	Potentiometric study on some protonated and non-protonated divalent metal ion complexes with α-furan-2-aldoxime	160

cont. Table 5.

SOLVENT	SUBJECT	Ref.
60% aqueous dioxane	Studies on metal chelates of 2-hydroxy-5-methyl-acetophenoneanil	161
75% aqueous dioxane	Formation constants of the divalent metal ion complexed of 2-hydroxy-1-napthalidene- α -naphthylamine	162
70% aqueous dioxane	Stability constant data of Cu and Ni chelates with some substituted 4-pyrazolone dyes are given and discussed	163

Table 6. Equilibrium constants of organic compounds

SOLVENT	SUBJECT	Ref.
tert-butanol	Dissociation constants are given for perchloric acid, picric acid, 2,4-dinitrophenol and benzoic acid	164
aqueous acetone, DMSO	The variation of the relative dissociation of acetic and benzoic acid was studied in 4 biner systems	165
ethylene glycol	The pK values of some acid-base indicators are reported	166
DMSO	Studies made on acid-base equilibria of a series of diazonium salts	167
sulpholane, AN	Comparison of provisional dissociation constants of some acids in the two solvents	130
acetic acid, AN, acetone	Dissociation constants are given for some organic salts	168
water-DMSO mixtures	Ionization constants of benzoic acid at different water content are reported. The ΔH° and $T\Delta S^\circ$ values for the ionization process have been also calculated	169
nitromethane	Ionization constants of 57 aliphatic and aromatic amines were determined	43
50% aqueous acetone	pK values of naphtalene derivatives were determined and investigated	170
methyl ethyl ketone	The ionization constants of numerous organic acids are reported	171
DMF	The dissociation of malonic, succinic and dimethyl malonic acid was studied	172
aqueous glycerol	The solvation of Na^+ and Cl^- ions were investigated in comparison with the results obtained in ethylene glycol	49
water-n-PROH mixtures	Dissociation constants and metal chelate stabilities of picolin and picolinic acids are studied in the range of $\epsilon = 30-80$	30
benzene-acetonitrile biner systems	pK_a and half-neutralization potential data are reported in the case of numerous organic compound	31
water-methanol biner systems	Ionization constants of p-substituted phenols are reported and studied	32

cont. Table 6.

SOLVENT	SUBJECT	Ref.
benzene-nitrobenzene benzene-nitromethane benzene-AN biner systems	Correlation between the half neutralization point and pK_a values were investigated	33
aqueous MeOH, EtOH, acetone biner systems	The hydrolysis of berillium ion was studied in mixed solvents	149
aqueous methanol mixtures	pK data are given for 8 p-substituted pyridinium ion	34
water-aliphatic alcohol mixtures	A method is reported for the determination of pK values in amphiprotic solvents	173
acetic acid, acetone MeOH	Dissociation constants of some aminobenzolides	174
DMSO	Dissociation constants of 6-substituted purine derivatives are given	175
80% aqueous DMSO	pK values of aliphatic mono carboxylic acids are reported	176
n-PrOH, tert-butanol	Dissociation constants of malonic, succinic, maleic and phtalic acids and of their methyl esters were determined	133
80% aqueous DMSO	pK values of some aromatic carboxylic acids are listed	177
dioxane-water	Ionization constant values of some quinolinol derivatives were determined	178
nitromethane	Acid-basic properties of hydroxypyridine derivatives were investigated to determine their structure	179
water-DMF, water-dioxane	Protonation contants of substituted benzoyl hydrazines were determined	180
acetone	pK values of picric acid and some acid-base indicators were determined	181
50% aqueous EtOH	The dissociation constants of some N-aryl hydroxa-mic acids were described	182
dioxane-water biner systems	Dissociation constants of some methoxybenzoic acid derivatives were investigated	183
PC	Determination of the ionization constants of 18 organic compounds are described	184
AN, DMSO dioxane-water	pK values of some sulphophtaleine derivatives are listed	185
90% aqueous N-methylacetamide	The problem of solvation of HCl was investigated on the basis of thermodynamic parameters	48
DMF	pK values of R-saturated dicarboxylic acids are given compared with those obtained in water	186
nitromethane, AN, DMSO	pK values of some NH- and OH acids are listed	42
AN	Ionization constants of 21 phenol derivatives are given	187
nitromethane	pK values of phenol and 9 mono-, di- and trisubstituted phenols are described	188

cont. Table 6.

SOLVENT	SUBJECT	Ref.
AN, acetone DMF, DMSO	pK values of 2,4,6-trinitrophenol are given	189
aqueous AN	Hydrolytic constants of tallium(III)ion are described, and the thermodynamic parameters of the hydrolytic process were evaluated	190
aqueous EtOH	Critical study of potentiometric methods for determination of some substituted benzamides acidity constants	37
PC	Dissociation constants of some protonated amines are given	191
dioxane-water bimer systems	The acidic dissociation of some N-arylhydroxamic acids were investigated	192
80% aqueous DMSO	pK values of 10 acid-base indicators were determined	193
80% aqueous 2-methoxyethanol	Dissociation constants of the E- and Z- α,β -di-arylacrylic acids are investigated	194
2-methoxyethanol	pK _a and pK _b values of 20 purine and pyrimidine derivatives were studied	195
MeOH, acetone, DMF, DMSO	pK values of 22 flavonoids were determined and compared with those obtained in water	196

Table 7. Determination of organic acids

SOLVENT	SUBJECT	Ref.
tert.-butanol	A method was developed for the evaluation of the dissociation constant of weak acids. Data are reported	164
MeOH-water, MeOH, acetone, EtOH	Potentiometric titration of weak acids with strong bases employing glass/calomel and Mo/Ag electrode systems	197
alcohols, ketones, AN	Titration of organogermanium compounds with KOH or K-methoxyde as titrants	198
DMSO, 1:10 DMSO + iso-PrOH	Titration of fulvic acid in ammonical and aqueous acetone extracts	199
dichlorometane	Titration of rosin with KOH	200
AN	Potentiometric titration method for the determination of 4-hydroxybenzoyl and alkylhydroxy-isophthalic acids with N-tetraethylammonium hydroxyde as a titrant	201
DMSO + methylamine + ethanolamine	Potentiometric titration of carboxy-groups in cellulose and its derivatives with Na-methoxyde in dimethyl sulphoxyde as titrant	202
1:2 acetone + benzene, 1:2 acetone + chloroform, 1:2 tert.-butanol + carbon tetrachloride, 1:2 2-hexanone+chloroform	Potentiometric analysis of formic and butanoic acids in mixed solvents with KOH titrant in different solvents	203

cont. Table 7.

SOLVENT	SUBJECT	Ref.
tert.-butanol	The use of tert.-butanol as differentiating solvent for the titration of some organic acids has been evaluated	328
1:3 iso-PrOH + dioxane	Potentiometric titration of diketones with KOH in isopropanol as titrant	204
AN + benzene in different ratios	Titration of organic acids and acid mixtures, HNP and pK _a data are given in the range of $\epsilon = 5-35$	31
AN, butanone	Determination of sulphanilamide preparations by potentiometric titration with KOH in different solvents	205
50% aqueous EtOH, acetone	Determination of inorganic acids and phenols in the presence of heavy pyridine bases by potentiometric titration	206
75% aqueous MeOH	Differential potentiometric titration of 2-ethylhexylphosphoric acid	207
50% aqueous acetone	pK _a -values was determined of substituted naphthols by potentiometric titration	170
ethylmethyl ketone	Determination of pK _a -values of some organic acids by potentiometric titration with tetraethylammonium hydroxyde as titrant	171
DMSO + water mixtures in different ratios	The pK _a values of benzoic acid increase with increasing dimethyl sulphoxide concentration of the solvent	169
DMF	Ionic equilibrium of malonic, succinic and dimethylmalonic acids was investigated	172
acetone, tert.-butanol	Potentiometric titration of mixtures of halo-substituted aliphatic monocarboxylic acids with K-isopropylate in isopropanol as titrant	208
acetone	Determination of pyromellitic, trimellitic and benzophenonetetracarboxylic acids using triethylamine as titrant	209
aqueous acetone	Potentiometric titration of acetic acid with alcoholic KOH as titrant in the presence of HCl	210
DMF	Potentiometric microtitration of phenols, carboxylic and phenolic acids with Na-methoxyde in DMF	211
benzene+ MeOH	Titration of β -lactam antibiotics with tetrabutylammonium hydroxyde as titrant	212
10-90% MeOH + water mixtures	Investigation of pK _a values of 4-substituted phenols by potentiometry	32
benzene + nitrobenzene benzene-nitromethane benzene-acetone	pK _a values of a series of acids are given: relationships between the pK _a and the half neutralization point were determined	33
glacial acetic acid, DMF, AN	Titration of some 1,4-benzodiazepines with tetrabutylammonium hydroxyde in 10% methanolbenzene as titrant	213
DMF	Differentiating potentiometric titration of aspirin, acetaminophen and salicylamide mixtures with tetrabutylammonium hydroxyde standard solution	214

cont. Table 7.

SOLVENT	SUBJECT	Ref.
methanol+water mix- tures	pK values and dissociation enthalpies of p- -substituted pyridinium ions are given	34
DMF	Potentiometric titration of intermediates of orotic acid syntheses with tetraethylammonium hydroxyde as titrant	215
acetone	Potentiometric determination of orotic acid in mixtures with its derivatives	216
isobuthyl-methyl ketone	Potentiometric titration of p-toluic and terephthalic acids and methyl terephthalate with tetrabutylammonium hydroxyde in isopropanol as titrant	217
EtOH	Potentiometric determination of 4,6-dinitro-o- -cresol in the technical grade product with KOH in ethanol as titrant	218
pyridine, ethylene diamine	Differential potentiometric titration of binary and ternary mixtures of benzanilides with a benzene + methanol solution of tetraethylammonium hydroxyde	219
80% aqueous DMSO	Titration of aliphatic mono carboxylic acids	176
5:1 benzene-EtOH	Separate determination of thioglycolic and dithio-220 glycolic acids by potentiometric titration	
DMF, acetone, pyridine tetramethyl guanidine, DMSO	Determination of benzotrioxifuran by potentiomet- 221 ric titration with tetrabutylammonium hydroxyde	
acetone, ethylmethyl ketone, DMF, iso- butyl-methyl ketone, AN	Potentiometric titration of some acid triphenyl- 222 methane dyes with tributyl-methylammonium hydroxyde in benzene-methanol (10:1) as titrant	
2-ethylhexanol, iso- dodecyl alcohol	Titrimetric determination of mixtures of higher 223 aldehydes and acetals as impurities in 2-ethyl- hexanol and in <u>i</u> sododecyl alcohol after oximation via liberated H ⁺ ions	
tert.-butanol, DMSO	Potentiometric titration of succinic acid with 133 methanolic tetraethylammonium hydroxyde as tit- rant	
80% aqueous DMSO	Potentiometric titration of some aromatic carboxy-177 lic acids	
50% aqueous tributyl phosphate, 50% aque- ous butyl acetate	Titration of weak carboxylic acids in the presence 224 of HCl	
aqueous dioxane	Potentiometric titration of 2-hydroxy-oxime 225 extractants	
DMF, DMSO	Potentiometric behaviour of extracted humic acids 226	
aqueous DMF and di- oxane	Potentiometric titration of p-substituted benzoyl 180 hydrazines to determine the pK _a values	
acetone	Determination of dissociation constants of picric 181 acid by direct potentiometric method	
50% aqueous EtOH	Potentiometric study of some N-aryl hydroxamic 182 acids	

cont. Table 7.

SOLVENT	SUBJECT	Ref.
50% aqueous acetone	Determination of sulphamerazine and sulphaproxyline in tablets by differential potentiometric titration	227
dimethyl acetamide	Potentiometric titration of phenolic end groups in monomeric and macromolecular structures	228
80% aqueous acetone	Determination of phenylbutazone by potentiometric titration	229
acetone, AN	Potentiometric titration of carbazole and nitrocarbazoles	230
Pyridine, tetramethylguanidine, hexa-methylphosphoramide	Potentiometric microtitration of 1,3,5-trinitro-1,3,5-triazacyclohexane and its derivatives	231
DMF	Potentiometric titration of some saturated dicarboxylic acids	186
nitromethane	Potentiometric titration of 3,5-dinitrobenzoic acid were carried out to study the solvation	42
AN	Potentiometric study on the effect of alkylthio group on phenols	187
iso-PrOH	Potentiometric titration of fumaric, maleic acids and maleic anhydride	232
nitromethane	Study on acid-base properties of substituted phenols by potentiometric titration	188
AN, acetone, DMF, DMSO	Potentiometric titration of 2,4,6-trinitrophenol in methanol-benzene mixtures. pK_a data are given in different solvents	189
tert.butanol	Determination of substituted benzophenone oxime reagents used in copper extraction processes	233
DMF, acetone, acetic acid, and their mixtures	Differential potentiometric titration was developed for determining nitroaminobenzanilides	234
10-50% aqueous dioxane	The acid dissociation of some N-aryl-hydroxamic acids were investigated by potentiometric titration	192
80% aqueous DMSO	Potentiometric titration of 10 acid-base indicators	193
80% aqueous 2-methoxyethanol	On the basis of potentiometric titration of E- and Z- α,β -diarylacrylic acids was studied the structure of 36 compounds	194
1:1 iso-PrOH-benzene	Potentiometric determination of 1,2,3-benzotriazole and N-hydroxy-1,2,3-benzotriazole is given	235
(0,4-0,57): 0,31 EtOH-benzene, 0,58:(0,02-0,12) xylene-water	Quantitative potentiometric determination of organic acids or their anhydrides	236
1:14 water-nitromethane	Potentiometric analysis of mixtures of some amino acids with their N-tert.-butoxycarbonyl derivatives	237
1:24 formic acid-ethylmethylketon 1:8 acetic acid-ethylmethylketon	Determination of binary mixtures of amino acids is described	238

cont. Table 7.

SOLVENT	SUBJECT	Ref.
acetone	Potentiometric determination of acidic impurities in 1,2-naphtoquinone-2-diazide-5-sulfonyl chloride is given	239
acetone	Determination of hydroxamic and carboxylic acids in a flotation agent was developed	240
DMF	Indirect potentiometric titration for determination of maleic anhydride by the morfoline method	241
1:(4-5)N-methyl-2-pyrrolidinone-PC	Quantitative determination of dicarboxylic acids is described	242
aqueous iso-PrOH-heptane systems	Quantitative determination of organic acids or their anhydrides	243
iso-PrOH	Determination of phthalimide and potassium phthalimide in technical grade mixtures	244
2-methoxyethanol	Potentiometric differential titration of purine and pyrimidine derivatives	195
23:7 DMF-benzene	Potentiometric determination of 5,5-dimethylhydantoin in reaction mixtures	245
acetone	Potentiometric titration of an isodithiobiuret derivative with different standard solutions	247
1:8 EtOH-benzene	Method for determination of acid number of mineral oils	246
chloroform-water	H_2A^+ type diprotic acids can be titrated in two-phase systems with good results	248
tert.-butanol, pyridine, acetone and iso-PrOH	The use of tetrabutyl ammonium hydroxide as titrant for weak and very weak acids is discussed	329

Table 8. Determination of organic bases

SOLVENT	SUBJECT	Ref.
acetic anhydride	Determination of m-toluic diethylamide by potentiom. titration with $HClO_4$ in dioxane as titrant	249
butanone	Mixtures of aminophenazone with Na-barbital, Na-phenolbarbital, Na-benzoate and Na-salicylate were determined with $HClO_4$ stock solution	250
1:1 acetic anhydride-acetic acid 1:1 acetic anhydride-dioxane 3:10:10 propionic acid-propionic anhydride-benzene	Differential potentiometric titration method was developed to determine codeine phosphate and some drugs in mixtures	251
2-butanone-benzene	Analysis of some ingredients of rubbers by potentiometric titration	252
MeOH, MeOH-DMF	Determination of some antibiotics is given by potentiometric titration	253
50% aqueous EtOH or acetone	Potentiometric titration of heavy pyridine bases	206

cont. Table 8.

SOLVENT	SUBJECT	Ref.
1:2:1 chloroform-AN-acetone	Potentiometric titration method for determination of amidopyrine, quaiacyl-o-hydroxybenzoate nicotinate and lidocaine HCl	254
1:1 acetic acid-trichloromethane	Potentiometric titration of methaqualone and its dosage forms	255
iso-PrOH, AN	Determination of sulphonylamide preparations by potentiometric titration	205
acetic anhydride	Potentiometric titration of 36 different phenothiazine derivatives	256
nitromethane	Study of basicity of aliphatic and aromatic amines by potentiometric titration	170
acetic acid-dioxane	Indirect potentiometric titration of hydrochlorides of nitrogenous bases	257
acetic acid, DMF, AN	Study of nonaqueous potentiometric titration of 1,4-benzodiazepines	213
acetic acid	Study on the chemistry of potentiometric titration of chlorpromazine	258
90% aqueous phenol	Determination of organic bases by potentiometric titration	259
acetic acid	Potentiometric titration of β -lactam antibiotics	212
dioxane	Determination of adenosine by potentiometric titration	260
acetic acid, acetone, MeOH	Potentiometric titration of some aminobenzolides	174
acetic acid, MeOH, pyridine, 1,1,3,3-tetramethylguanidine	Investigation of the standardization of standard solutions using in nonaqueous titrimetry	261
nitromethane	Potentiometric titration of dipiperidylbenzaminals	262
1:2:4 chloroform-acetic anhydride-benzene	Potentiometric titration of caffeine	263
acetone	Potentiometric titration of triphenyltin compounds	264
nitromethane	Determination of dipiperidylbenzaminals	265
dioxane	Potentiometric titration of 2-hydroxyoximes	225
nitromethane	Potentiometric titration of hydroxypyridine derivatives	179
acetic acid	Improved method for potentiometric titration of salts of organic bases by adding $\text{Bi}(\text{NO}_3)_3$	266
acetic anhydride	Micro-determination of nitroguanidine by potentiometric titration	267
2-methoxyethanol	Determination of 6-benzylaminopurine by potentiometric titration	268
nitromethane	potentiometric titration of some dipiperidyl derivatives in piperidine	184

cont. Table 8.

SOLVENT	SUBJECT	Ref.
acetic acid	Potentiometric titration of several amine salts	269
20-80% aqueous AN, MeOH, dioxane	Potentiometric titration of nicotinyl and benzoyl hydrazines	135
aqueous EtOH	Potentiometric titration of some substitutes benzamides	37
PC	Potentiometric determination of several protonated amines	191
dioxane	Method is given for determination of Na-salicylate, amygdopyrine and caffeine and their mixtures in Pyrosalofen tablets	270
acetic acid	Potentiometric titration of nitro-aminobenzanilides	234
aqueous EtOH, dioxane	Potentiometric determination of difurfuralidin-acetone	271
80% aqueous DMSO	Potentiometric titration of 10 acid-base indicators	193
1:1 nitrobenzene- -chloroform	Potentiometric titration of Katamin AB in mixtures with rosin and terpentine with picric acid	272
2-methoxyethanol	Potentiometric differential titration of pyrimidines and purines	195
acetone	Analysis of 4,4'-diamino-3,3' dihydroxydiphenylmethane by potentiom. titration	273
ethylmethylketone	Evaluation of titration method of C ₁₆₋₁₈ alkylpropylamines is improved by the use of Gran method	274

Table 9. Determination of inorganic compounds

SOLVENT	SUBJECT	Ref.
1:1 DMF + iso-PROH	Differentiated titration of Sc, Y and La salts with KOH in isopropanol	28
acetone	Analysis of KCl, H ₂ SO ₄ , KNO ₃ and K ₃ PO ₄ by potentiometric titration	275
15:15:2 acetic an- hydride-acetic acid- -formic acid	Determination of alkaline nitrates	276
MeOH, EtOH, acetone ethyl-methyl keton, 3:1 MeOH-acetone	Determination of H ₂ TiCl ₆ and H ₂ TiF ₆ in the presence of HCl and HF by potentiometric titration	277
aqueous acetone	Determination of HCl and acetic acid in the presence of ion(III)	210
aqueous MeOH	Indirect titration of sodium sulphate in anionic surfactants	278
aqueous MeOH	Determination of fluorophosphoric acids and their mixtures with other inorganic acids	279
acetone, iso-PROH, ethyl-methylketon	Differentiated titration of a mixture of ammonium perchlorate with perchloric and hydrochloric acids	280

cont. Table 9.

SOLVENT	SUBJECT	Ref.
iso-PrOH, tert.-butanol, n-hexanol	Study on acid-base equilibria of HCl and HBr	47
PC	Potentiometric study of protonation of water in comparison with other methods	281
1:1 ethylene glycol-acetone	Determination of sulphuric acid and ethyl sulphate	282
alcohols, ketones nitromethane	Study of acid-base properties of Nb, Ta, V, Mo and VO ₂ chlorides	284
3:2 acetone-trichlorometane, acetone-sec. butylchloride	Determination of HCl and iron(III)chloride in hydrochlorination processes	283
1:(7-25) water-acetone	Determination of sulphuric acid and sulphonic acids in mixtures	285
acetic acid	Determination of boric acid	286
acetone	Determination of sulphuric acid in a mixture	287
acetone	Determination of phosphoric acid in a reaction mixture	288

Table 10. Determination of organic and inorganic compounds in their mixtures

SOLVENT	SUBJECT	Ref.
50% aqueous EtOH or acetone	Determination of heavy pyridine bases in the presence of inorganic acids or salts	206
aqueous acetone	Determination of HCl and acetic acid in a mixture by potentiom. titration	210
50% aqueous tributyl phosphate or butyl acetate	Potentiometric titration of weak carboxylic acids in a mixture with HCl	224
EtOH	Determination of L-carnitine HCl in the presence of NH ₄ Cl	289
chlorobenzene-acetone biner system	Determination of S ₂ Cl ₂ in mixtures with phthalimid, potassium phthalimide and N,N'-dithiobis(phthalimide)	290
1:1 ethylene glycol-acetone	Determination of sulphuric acid, and ethylhydrosulphate in a mixture	282
3:2 acetone-trichloromethylmethane or acetone- sec. butyl chloride	Determination of HCl and iron(III) chloride in the presence of organic compounds	283
1:(7-25) water-acetone	Quantitative determination of sulphuric acid and sulphonic acids in a mixture	285

Table 11. Cation-selective glass electrodes

SOLVENT	ION MEASURED	SUBJECT	Ref.
AN, PC and DMF	K^+ , Na^+ , Li^+ K^+	The Beckman 39047 electrode was studied after etching in solution of the measured ion in the appropriate solvent. Lifetime, response and stability data are given	51
AN, DMF, DMSO	K^+	The response time, reproducibility of the Beckman 39047 electrode are reported	52
AN, DMSO	Na^+		
AN	Rb^+ , Tl^+ , NH_4^+ , Cs^+	The response of the Beckman 39047 electrode was investigated	53
PC	Li^+	The response characteristics of the Beckman 39137 electrode and selectivity data in the presence of K^+ , NH_4^+ and Et_4N^+ ions	54
MeOH, AN PC, DMSO	K^+ , Tl^+ ; Na^+	Response characteristics of a K^+ and a Na^+ -sensitive electrode are investigated and applied to study the complex-formation of some macrocyclic polyethers with Na^+ , K^+ , Rb^+ , Cs^+ and Tl^+ ions	55
MeOH	Na^+ Na^+ , Li^+ , K^+ , Cs^+ NH_4^+	Complex formation was studied with macrocyclic polyethers	105
AN	Na^+ , Li^+	Thermodynamic data of some macrocyclic compound complexes were determined	106
AN	Li^+ , Na^+ , K^+ , Rb^+ , Tl^+ , NH_4^+	A brief study of complexation of univalent ions with a series of solvents e.g. MeOH, DMF, etc., by a Beckman 39047 electrode	108
PC	Na^+ , Li^+	Complex formation of ions with dimethyl sulfoxide was investigated	111, 112
MeOH, EtOH, n-PrOH, n-BuOH n-pentanol, n-heptanol, n-octanol	Na^+ , I^-	The mean activity coefficient of ions was determined using a Na^+ -selective glass electrode Radelkis OP-Na-711 D	79-86
liq. ammonia	NH_4^+	Measurement were made by a Beckman 39137 type cation-sensitive glass electrode	113
fused ammonium nitrate	univalent and some divalent cations	The response of a Pyrex bulb electrode at 190 C° was studied	67, 115
various organic solvents		Determination of free energy of transfer of alkali metal chlorides	56, 57
different solvents e.g. AN, PC etc.	K^+ , Li^+ , Na^+ , Rb^+ , Cs^+ , Tl^+ , Ag^+	The response of the Beckman 39047 electrode was studied	63
different solvents		Studied made on the selectivities of cation-sensitive glass electrodes	50, 51, 67, 68
aqueous methanol		Investigation of transfer of alkali fluorides and chlorides from water to aqueous methanol using several glass electrodes as reference. The specific solvent affect of the latter was also studied	87

Table 12. Application of fluoride ion-selective electrode

SOLVENT	SUBJECT	Ref.
60% aqueous EtOH	Condition of potentiometric titration of fluoride ion with Th(IV)-, La(III)- and Ca(II) -ions in aqueous ethanol is presented	91
60-70% aqueous EtOH	Potentiometric titration of fluoride ions by lanthanum ions as titrant. The organic solvent gives better results than the unbuffered aqueous media	92
DMSO	The titration curves taken by a fluoride-selective electrode did not give satisfactory results in this solvent	93
80% aqueous EtOH	A method is described for rapid determination of organically bonded fluorine after combustion	291
50% aqueous EtOH	Microdetermination of fluorine content of organic compound containing phosphorus is given. After combustion the fluoride ion was titrated with La(III)	292
30-70% aqueous EtOH	Determination of Si, Al, Fe, Ca and Mg with a fluoride ion selective electrode is reported by an indirect titration method	293
50% aqueous MeOH, 60% aqueous iso-PrOH	Direct measurements as well as titrations of fluoride ion with La(III) using a fluoride ion-selective electrode	294
20, 40, 60, 80% aqueous dioxane	The formation constants of HF and (HF) ₂ were determined using a fluoride ion-selective electrode	295
50% aqueous (EtOH, iso-PrOH, acetone DMF, AN), dioxane	The Orion and a self-constructed LaF ₃ (doped with SrF ₂) fluoride ion-selective electrode were investigated, both by direct and indirect potentiometric technique. A procedure for titration with thorium nitrate is given. The best media for the electrode is the 30% dioxane-water composition. Inorganic and organic fluorine compounds were determined, resp.	296
80% aqueous EtOH	The potentiometric titration of Al(III)-La(III)- and Th(III)- ions is described by using a fluoride ion-selective electrode	297
MeOH-water biner systems	A method is given for the determination of methanol content in biner systems using ion-selective electrodes	298
water-(MeOH, EtOH, PrOH, acetone, dioxane) biner systems	Determination of fluoride ion by direct potentiometry in organo-aqueous biner systems	136
aqueous EtOH	Determination of fluoride ion content in Sn(II)-Ni(II) electrolytes with a CuF ₂ doped LaF ₃ electrode is described	299
40-90% aqueous acetone or EtOH	Determination of sulphate ions by potentiometric titration using Ba(II) as titrant in the presence of known amount of sodium fluoride	120
80-90% aqueous EtOH	Indirect titrimetric determination of tungsten and phosphorus via titration of excess sulfate ion after precipitation with Ba-salt, filtration, finally addition of known amount of sodium sulfate	300
MeOH, aqueous MeOH	Determination of stability of alkaline earth monofluoride complexes	121
MeOH, EtOH, PrOH acetone, dioxane	Titration subnanomole quantities of fluoride of fluoride with La ³⁺ is described	119
aqueous acetone or EtOH	Determination of sulfate ions with Ba ²⁺ in the presence of known amount of sodium fluoride is given	120

Table 13. Response of fluoride ion-selective electrode in various solvents (96)

solvent	slope for 3 <pF> 5	slope for 5 <pF> 6	lower limit of usable range, pF
H ₂ O	58.1	x	6.0
MeOH	62.0	90	6.8
MeOH+1 mol% H ₂ O	59.5	60	6.7
MeOH+10 mol% H ₂ O	59.3	58	6.5
EtOH	64.0	80	7.0
EtOH+1 mol% H ₂ O	59.5	71	6.3
EtOH+ 10 mol% H ₂ O	59.0	63	6.7
1-PrOH	65.0	101	6.0
1-PrOH+1 mol% H ₂ O	62.5	80	6.5
1-PrOH+10 mol% H ₂ O	61.0	77	6.5
2-PrOH	66.0	x	5.0
AN+10 mol% H ₂ O	57.8	x	5.6
PC+10 mol% H ₂ O	62.0	62	6.5

*Slope gradually changed to less negative values with this region.

Table 14. Application of silver sulfide ion-selective electrode

SOLVENT	SUBJECT	Ref.
74% aqueous acetic acid	Automatic titration method is presented for the determination of small amounts of halogenides	301
80% aqueous acetic acid	A semi-automatic halogen determination is described for organic compounds after decomposition by argentometric titration	302
70% aqueous MeOH or acetic	Titration method is proposed for determination of water-insoluble mercaptans with silver ions as titrant	303
80% aqueous acetic acid	Microdetermination of organically bonded chlorine and bromine in volatile compounds after combustion is described	304
EtOH-benzene biner system	A method is given for determination of hydrogen sulfide and thiols in petroleum products by potentiometric titration	305
90% aqueous EtOH	Argentometric titration method is proposed to determine the radiolytically produced chloride content in chlorobenzene solution	306
MeOH-water biner system	A method is described for the determination of methanol content in biner aqueous system	298
MeOH	Potentiometric titration method for determination of some tetrazoles	307
20% aqueous glycerol	A method is given for determining H ₂ S content in air samples after absorbing by standard addition technique	308
30% aqueous acetone	Determination of some metal ions using sulphur-containing organic reagents by potentiometric titration method	309
EtOH	Potentiometric titration is described for determination of captax	310

cont Table 14.

SOLVENT	SUBJECT	Ref.
EtOH	A new sulfide ion-selective is proposed for determination of S^{2-} ion and thiourea. The electrode is a Pt coated wire with As_2S_3 electroactive material	144
80% aqueous acetic	Method is given for determination chlorine and bromine in volatile organic compounds	311

Table 15. Application of iodide ion-selective electrode

SOLVENT	SUBJECT	Ref.
MeOH, EtOH, n-PrOH, iso-PrOH and their mixtures with water	Determination of iodide ion by direct potentiometric method	76
aqueous MeOH, EtOH, n-PrOH iso-PrOH	Potentiometric titration for determination of iodide ion	77
methanol-water biner systems	A method is described for the determination of methanol content in its biner aqueous system	298
20% aqueous MeOH	Potentiometric titration of large inorganic and organic anions with quaternary ammonium halides	312
aqueous MeOH	Indirect potentiometric titration for determination of L-ascorbic acid, p-(methylamino)-phenol sulfate and hydroquinone after treating with iodide solution in methanol, then the iodide produced was determined	313

Table 16. Application of bromide ion-selective electrode

SOLVENT	SUBJECT	Ref.
n-butanol	Determination of bromo-content in organic compounds after combustion by potentiometric titration	314
methanol-water biner system	A method is described for the rapid determination of methanol content in MeOH-H ₂ O biner systems	298

Table 17. Application of chloride ion-selective electrode

SOLVENT	SUBJECT	Ref.
80% aqueous dioxane	Microdetermination of chloride in the presence of azide by potentiometric titration with mercury(II) perchlorate as titrant	315
AN	The titration of halide ions using a chloride-selective electrode only in the presence of oxidizing agents or strong acids gives satisfactory results	88
90-100% iso-PrOH	Direct potentiometric determination of a series of alkali- and alkaline earth metal chlorides and tetramethyl- and tetramethylammonium chlorides is given with 0,9% rel. error	89

cont. Table 17.

SOLVENT	SUBJECT	Ref.
50% aqueous dioxane	A potentiometric titration method is proposed for determination mixtures of alkali chloride and fluoride	296
tributyl phosphate	Potentiometric investigation of some metal chloro-complexes	316
formic acid	Kinetic studies on the rates of reaction of formolysis of benzoyl chloride and p-substituted benzoyl chlorides	317
3:2 acetone - dil.HNO ₃	Organic chloro-compounds were determined after decomposition by potentiometric titration with an chloride ion-selective electrode	318
methanol-water biner system	A method is described for the determination of methanol content in its biner aqueous system	298
aqueous acetone, iso-PrOH or ethyl methyl ketone	Determination of HCl content in a mixture of ammonium perchlorate, perchloric and hydrochloric acid	280

Table 18. Application of lead ion-selective electrode

SOLVENT	SUBJECT	Ref.
50% aqueous dioxane	Determination of sulphate ion by potentiometric titration using lead perchlorate as titrant	123
60% aqueous dioxane	Potentiometric titration method is described for determining sulphur content of organic compounds after combustion, via sulphate ion	124
50% aqueous MeOH	Determination lead in galvanic mixtures by potentiometric titration	319
50% aqueous MeOH	Potentiometric titration for determining of molybdenum with lead ions	
aqueous dioxane	Indirect determination of sulphate ion concentration in galvanic mixtures	
aqueous dioxane	Determination method is given for tungsten by titration with lead perchlorate as titrant	
50% aqueous acetone	A new PbS-Ag ₂ S electrode has been used for determination of sulphate ions by titration with lead nitrate standard solution	101
50% aqueous dioxane	Determination of trace sulphur in petroleum products by potentiometric titration	125
50% aqueous MeOH	Determination of lead content in paints	303
50% aqueous MeOH	Determination of sulphate by titration with lead ions	304
50% aqueous dioxane	Method is given to determinate the sulphate content in food colors by potentiometric titration with lead nitrate as titrant	320
70% aqueous EtOH	Comments on the determination of concentrated sulphate solutions by potentiometric titration with lead perchlorate	321

SOLVENT	SUBJECT	cont Table 18.	REF.
50-70% aqueous MeOH	Potentiometric determination of drug sulphates with lead perchlorate		322
aqueous acetone	Potentiometric determination of sulphate in white and green liquors. The use of acetone instead of ethanol gave better results		323
80% aqueous EtOH	Potentiometric method is given for determination of sulphur in secondary alumina after combustion with a newly developed lead selective electrode		384
aqueous MeOH	Determination of sulphur content in organic compounds by potentiometric titration		325

Table 19. Application of copper ion-selective electrode

SOLVENT	SUBJECT	REF.
MeOH, acetone, AN	Direct potentiometric method and complexometric titrations of copper(II) ions with several ligands are presented	97
50% aqueous acetic acid	Some hydrazines were titrated with copper(II) ions	326
45% aqueous EtOH	Direct potentiometric titration of copper(II) ion with EDTA in the presence of iron(III) ions	327

Abbreviations

MeOH	methanol
EtOH	ethanol
n-PROH	n-propanol
iso-PROH	isopropanol
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
PC	propylene carbonate
AN	acetonitrile

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