

Review

Natural Sulfide Minerals as Electrode Materials for Electrochemical Analysis in Dipolar Aprotic Solvents

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Dipolar aprotic solvents are compounds with the relative permittivity higher than 15 and a dipole moment greater than 2 D. Solvents of this type are applied in the field of kinetic, catalytic and electrochemical studies. Many organic molecules with high molecular weight are readily dissolved in dipolar aprotic solvents. These solvents have relatively high pK_S and wide-area working potential which allows the determination of a large number of compounds in them. This review was written to provide the insight of electrochemistry in non-aqueous solutions, primarily based on the characterization and application of some solid-state sensors in a non-aqueous environment. Firstly, it highlights the results obtained over many years of investigation in our laboratory with the aim to contribute to the development of pure and applied chemistry in non-aqueous solutions. The review is divided into two main parts. The first part contains a discussion of solvent properties which further basically determine their application in electrochemistry. Second part mainly deals with the characteristics and use of the natural sulfide minerals (pyrite, chalcopyrite, and arsenopyrite) as electrochemical sensors in non-aqueous solutions for different purposes.

Keywords: Natural minerals; Pyrite, Chalcopyrite; Arsenopyrite; Sensor

1. INTRODUCTION

Most chemical reactions are carried out in solutions. The application of a solvent as a reaction medium allows easy control of the reaction conditions such as temperature, pressure, pH, and reactant concentration. In the recent decades, the application of non-aqueous solvents, especially dipolar aprotic solvents (DASs), in various fields of fundamental and applied chemistry has been largely presented, which significantly contributes to the further development of chemistry and technology [1]. Using non-aqueous solvents allowed many new electrochemical technologies to be developed. From the very

beginning, electrochemistry in non-aqueous solutions played an important role in predicting the effect of solvents on various chemical processes and the properties of dissolved electrolytes. Water-insoluble substances can be dissolved by using suitable non-aqueous solvents. Additionally, the stability of the substances can increase and the chemical reactions that are impossible in the aquatic environment can be performed. The comments of some authors in their recent studies also go in favor of the importance of non-aqueous solvents in the various fields of research: “Given that protein dynamics are significantly attenuated in organic solvents and that proteins exhibit a wide range of motions depending on the specific solvent environment, the non-aqueous milieu provides a unique opportunity to examine the role of protein dynamics in enzyme activity” [2].

The sensitivity and accuracy of the determination of substances in a non-aqueous environment depend on the sensitivity of the method/sensor for their detection. In addition to its undeniable value, the most commonly used electrode in potentiometric titration – glass electrode – has certain drawbacks such as mechanical sensitivity, limited lifetime, and the impossibility of successive application in non-aqueous solvents. In this regard, the further development of potentiometric methods was aimed at finding new sensors for the determination of titration end-points. Current research suggests that solid-state indicator electrodes without internal solution play an important role in chemical studies [3].

In this review, a potentiometric technique applied in non-aqueous solvents such as γ -butyrolactone, ethylene carbonate, propylene carbonate, acetonitrile, and propionitrile was considered. The basic properties of non-aqueous solvents have been identified, including the effect of solvents on electrolyte dissolution, ionic reactions, and equilibrium, with particular emphasis to acid-base, precipitate, and redox reactions in the above-mentioned non-aqueous solutions. Additionally, titrations in non-aqueous solutions have been considered, highlighting the overall importance of chemical sensors as well as the results of determination of various compounds in γ -butyrolactone, ethylene carbonate, propylene carbonate, acetonitrile, and propionitrile, with the application of electrochemical sensors – pyrite, chalcopyrite, and arsenopyrite indicator electrodes.

2. DIPOLAR APROTIC SOLVENTS

Aprotic solvents are chemically inert compounds that do not show a tendency to receive or release protons. These compounds have small dipole moments ($\mu = 1-2$ D) and small relative permittivity ($\epsilon_r < 15$). In aprotic solvents (e.g., benzene, carbon tetrachloride, chloroform, cyclohexanone), the hydrogen atom is bound to carbon, so there are poorly expressed proton donor-acceptor properties among the solvent molecules, as well as the possibility of making hydrogen bond. Aprotic solvents, having a relatively large dipole moment ($\mu > 2.5$ D), relatively high permittivity ($\epsilon_r > 15$), and belonging to a special group of aprotic solvents, are known as dipolar aprotic solvents.

Dipolar aprotic solvents, due to their physico-chemical properties (high value of autoprotolysis constants, differentiating effect, wide working potential range, liquid state in a wide temperature range), have become the subject of intensive both fundamental and applied investigations in the chemistry of non-aqueous solutions. This group includes most of the solvents used for investigation in our laboratory: nitriles (acetonitrile, AN; propionitrile, PN), nitro compounds (nitromethane, NM), as

well as cyclic esters (ethylene carbonate, EC; propylene carbonate, PC; γ -butyrolactone, γ -BL). Unlike protolytic solvents which participate in a reaction of protons exchange and in the reaction of forming a hydrogen bond, DASs are coordinating solvents able to act as a Lewis base.

Properly selected solvents allow the determination of the given substance under optimal conditions. In the process of solvents selection, donor numbers (DN), acceptor numbers (AN), autoprotolysis constants (pK_S), and relative permittivities (ϵ_r) are especially important (Table 1).

Table 1 Chemical properties of some of the organic solvents of electrochemical interest [1].

Solvent	DN	AN	pK_S	ϵ_r
Nitromethane	2.7	20.5	-	36.7
Acetonitrile	14.1	18.9	33.3	35.9
Propylene carbonate	15.1	18.3	-	66.1
Propionitrile	16.1	-	-	28.9 ₂₀ *
Ethylene carbonate	16.4	-	-	89.6
γ -Butyrolactone	18	17.3	-	39.0
Water	18(G)-33(L)**	54.8	14.0	78.4

* Unless otherwise stated, the data are at 25 °C. The temperature values other than 25 °C are shown as a subscript.

** G-gas, L-liquid.

The examination of the dielectric properties of dipolar aprotic solvents enabled us to resolve many issues related to the process of dissolution of the investigated substance, including the behaviour of the test substance in homo- and heteroconjugation, as well as reactions with the titration agent and other components in the solution. In the solvents of low relative permittivities ($\epsilon_r < 15$), the dissolved substance is poorly dissociated or even not dissociated, while in high permittivity solvents ($\epsilon_r > 15$), the dissolved substances are not only ionized but also dissociated. The mutual electrostatic attraction of the ion electrolyte ('ion association') leads to the formation of ionic pairs. The ion association has a great importance in analytical chemistry of non-aqueous solutions and it is directly related to the relative permittivity. Namely, in low-permittivity solvents, the ionic association is more intense, while in high-permittivity solvents, it can be completely absented.

2.1. Acetonitrile

Acetonitrile is one of the best-studied and most widely used solvents belonging to the DAS group, which dissolves both organic and inorganic substances very well; it mixes with water and it is in the liquid state in the temperature range from -45 °C to +82 °C [1]. The reactions of acid and base conjugation in acetonitrile occur with weak acids and bases at concentrations greater than 10^{-3} mol/L. With acetonitrile, strong acids and bases form the corresponding salts [1]. The proton donor-acceptor interaction between acetonitrile and dissolved acids takes place at a slow rate due to the weak polarity of the methyl group, unlike propionitrile, where, due to the π electrons, this process happens rapidly.

There are numerous papers in the literature which explain its application for various electrochemical investigations in the field of analytical chemistry [4,5]. Acetonitrile is one of the most widely used solvents for potentiometric acid-base titration [6-10].

2.2. Propionitrile

Propionitrile has a high vapor pressure at room temperature and is in the liquid state in a wide temperature range (from -92 °C to +97 °C) [1]. Its properties are like those of acetonitrile, so it is often used in a mixture with acetonitrile or instead of it. It is one of the solvents from the DAS group which is least frequently used for analytical determinations.

2.3. Nitromethane

Nitromethane shows poorly acidic properties [1]. In the temperature range from -28 °C to +101 °C, it is in the liquid state. In spite of the fact that it is a solvent with high relative permittivity, dissociation of salts is poorly expressed. In the nitromethane, a small number of inorganic salts are dissolved, so low salt solubility and the effect of water on the determination of the end-point of titration are its major disadvantages. Traces of water in the solvent prevent the determination of bases with $pK_a < 14$.

2.4. Ethylene carbonate

Ethylene carbonate is an ester of ethylene glycol and carbonic acid. At room temperature, it is a colorless crystal slightly soluble in water, while at the temperature of 34-37 °C, it turns into a colorless liquid. It is an extremely polar solvent; individually and in mixture with propylene carbonate, it is used as an electrolyte for lithium batteries [1]. Since it is in the solid state at room temperature, it is often used in mixture with water or with an organic solvent. It has been established that ethylene carbonate, as well as its related solvent – propylene carbonate – has working potential range of about 5 V, which is convenient for its application as a medium for electrochemical measurements [11]. In the mixture of solvents ethylene carbonate/propylene carbonate, the behavior of copper (II) salts was studied by applying the conductometry, potentiometry, and voltammetry [11], as well as the possibility of application of pH standards in these solvents mixed with water [12]. In order to optimize chemical and physico-chemical parameters such as viscosity, dielectric constant, dissociation constant, ionic conductivity, and ion activity, mixtures of acetonitrile + ethylene carbonate and ethylene carbonate + propylene carbonate were used [13,14].

2.5. Propylene carbonate

Propylene carbonate is a complex cyclic ester of 1,2-propylene glycol and carbonic acid. It is characterized by the high solubility of many organic and inorganic compounds but no toxicity, which expands its application in industry. In analytical chemistry, propylene carbonate is used as a medium

for titration and as an extragent. There is also a well-known and interesting study dealing with the propylene carbonate characteristics and conductometric determination of the acid dissociation constants in this solvent [15].

2.6. γ -Butirolakton

Owing to the high value of relative permittivity and low viscosity as well as the high solubility of a number of organic and inorganic compounds, it dissolves polyacrylonitriles, polystyrene, polyamides, and other polymers. The acid-base properties of this solvent are very close to the properties of propylene carbonate; it is most commonly used secondary electrolyte for lithium batteries [1,16].

To summarize, the pH window is very wide in all above-mentioned solvents that appear to be weak in both acidity and basicity. The widths of the pH window are well over 25 in these solvents, compared to about 14 in water. Potentiometric titrations in such expanded pH regions are highly useful in the practical chemical analysis along with physico-chemical studies, as will be discussed below.

3. FROM SULFIDE MINERALS TO SENSORS' MATERIALS

The solid membrane in the ion-selective electrodes can be selective to the anions in the same way as the glass membrane is selective on the cations. It is well known that the presence of anionic sites on the glass surface contributes to the selectivity of the glass membrane on the cations, which analogically suggests that membranes with cationic sites on the surface show selectivity towards the anions. For years, membranes made from silver halide have been successfully used to produce electrodes for the selective determination of Cl^- , Br^- i I^- ions. Electrodes with a sensor of some monocrystals proved to be selective for certain cationic and anionic species. One of these electrodes is pS and pAg selective electrode whose sensor was made from Ag_2S single crystal. The change of potential as a result of the change in the activity of the tested cation or anion in the solution can be detected using an ion-selective electrode that is coupled with the reference electrode through the test solution:

$$E = E^\circ \pm 0.059 / n \cdot \log a_A \quad (1)$$

where the plus sign corresponds to the cation and the minus sign to the anionic species. The Equation (1) represents the ideal response of the electrode to the tested ion activity when there are no interfering ions in the solution. In practice, such ideal selectivity of an electrode is not known. The range where an electrode shows the Nernst dependence is limited even in the solvents with the corresponding ions only.

Natural minerals, although poorly reactive and slightly soluble in water, can significantly change their surface layer under the influence of the environment and thereby to change their behavior in terms of reactivity, catalytic capacities, electrochemical conductivity, thermochemical stability, and others. The presence of other oxidants such as Fe(III)-ion, pH value, environmental temperature, and the presence of bacteria can also affect the state of the sulfide minerals surface.

Pyrite, FeS₂, natural iron(II) disulfide, is generally one of the most widespread sulfide minerals in nature. It is very often the ingredient of other sulfide ores and it can be separated as a byproduct after the processing of chalcopyrite, galenite, and sphalerite. Pyrite is crystallized by the cubic system and it is isomorphous with a crystalline system of NaCl where Na atoms are replaced by Fe atoms, while bivalent sulfur replaces chlorine. In most natural resources, it exists in the form of *p*-type semiconductors. Due to the importance of the surface oxidation in air and air-saturated aqueous solution of the iron sulfide mineral, pyrite was the subject of numerous studies, both theoretical and experimental, whereby different spectroscopic and electrochemical methods have been used [17,18].

Chalcopyrite, CuFeS₂, is the most widespread of copper sulfide minerals. It crystallizes in the tetragonal system and is isomorphic in the sphalerite structure. If it is a crystal without impurities, then chalcopyrite belongs to the *n*-type semiconductors. Types of products that occur during the oxidation process depend on a number of factors such as pH, properties of the oxidant, temperature, and properties and concentration of the present cations, anions, chelating agents, and other chemical species [19]. The creation of sulfur on the surface of the chalcopyrite due to passivation of the surface can slow down the dissolution of this mineral in the natural environment. In this case, the properties of the passive layer, as well as interactions on the surface of the minerals, can influence oxidation rates.

Arsenopyrite, FeAsS, an iron arsenic sulfide, is often the most abundant mineral in tailings of sulfide ores. Chemical and biological oxidation of arsenopyrite present in mining tailings results in the release of arsenic from minerals, thus making it one of the main pollutants produced by the mining industry [20]. For this reason, special attention is devoted to the simulation-based investigations of the exposure of minerals to various external, environmental conditions and chemical influences, including the electrochemical behavior of arsenopyrite under different current conditions [9].

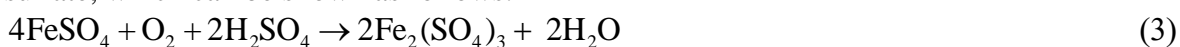
3.1. Properties of sulfide minerals as preconditions for their application in electrochemistry

3.1.1. Pyrite, chalcopyrite, and arsenopyrite

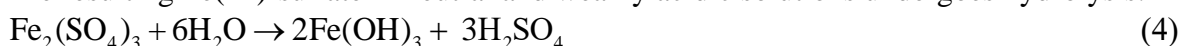
The oxidation of these minerals is very often studied in, above all, aqueous solutions, where the examination of the kinetics and the oxidation mechanism of pyrite under the action of ‘natural’ oxidants, such as oxygen, primarily take place [21]. The oxidation processes of these minerals can be most clearly shown by using pyrite as an example and in accordance with the considerations stated in the ref. [21]:



Fe(II)-sulfate is unstable in the presence of oxygen; it further undergoes oxidation and forms Fe(III)-sulfate, which can be shown as follows:



The resulting Fe(III)-sulfate in neutral and weakly acidic solutions undergoes hydrolysis:



When pyrite is oxidized in the presence of water, the acid, dissolved iron, and sulfate are produced, along with the release of heat [22]. In the first step, sulfate is built up (Equation 5), while in

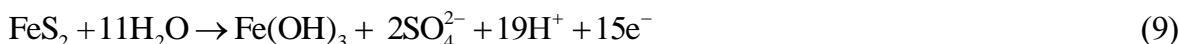
the second step Fe(II)-ion is oxidized into Fe(III)-ion (Equation 6). In summary, these processes can be represented by the Equation 7:



Formed products (Fe(III)-ions, as well as sulfuric acid) stimulate autocatalytic oxidation of pyrite.

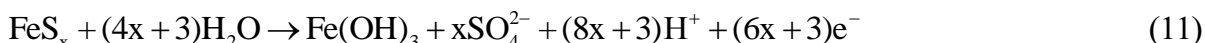
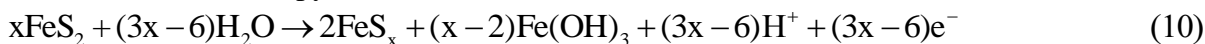
Electrochemical investigations of pyrite have greatly contributed to understanding the processes occurring on the surface of a mineral such as oxidation and other electrochemical aspects related to pyrite and other accompanying sulfides. The most commonly used technique is cyclic voltammetry, supported by other powerful ones such as SEM, XPS, and FTIR, applied for both the characterization of surfaces and of compounds formed on the surface of the mineral. To some extent, these studies helped to find out the mechanism of pyrite oxidation, although it has not been completely defined. Oxidation of sulfide minerals is an extremely complex process, so the conclusions of the researchers vary, as can be seen in further examples.

- Electrochemical oxidation of pyrite leads to the formation of elemental sulfur and sulfate and the following reactions take place, as Hamilton and Woods point out [23]:



The authors believe that elemental sulfur appears as a monolayer and that the oxidation of sulfide sulfur in sulfate is the dominant reaction. Also, they believe that the amount of sulfate grows with the increase of anodic potential, along with the ubiquitous Fe(III)-hydroxide, which is generated in accordance with the reactions (Equations 8 and 9).

- Similar conclusions were made by other authors [24] by using cyclic voltammetry and the characterization of the pyrite surface after its oxidation:



The presence of elemental sulfur, polysulfide, sulfate ions, and iron(III)-hydroxide has been confirmed by Raman spectroscopy.

- Based on the ionic species determined in the solution, Fornasiero and co-workers [25] observed oxidation of pyrite as a stepwise process which, in addition to the separated sulfur, anodic oxidation Fe(II)-ion into Fe(III)-ion, and the cathodic reduction of oxygen, also includes hydrolysis of Fe(III)-ion, which can be traced through several hydroxide forms:



Under normal conditions, iron(III)-hydroxide (Equation 17) is slowly degraded to thermodynamically stable forms, such as goethite, magnetite, and hematite.

From this brief overview presenting heterogeneous approaches to the consideration of pyrite oxidation, this process can be comprehended in its complexity, and, consequently, has not been fully elucidated yet. What is common to all the approaches of pyrite oxidation process taken into account is that iron(III)-hydroxide is separated in all cases.

In accordance with the previous studies [26], the complex oxidation process of chalcopyrite involves the formation of sulfur and sulfates (Equations 18 and 19).



In addition to the above components, there are copper and iron ions prone to hydrolysis (similar reactions as the ones represented by Equations 13-17).

Oxidation of arsenopyrite with available oxygen [9] is described by the following chemical equation:



Arsenic, separated in the form of arsenic acid, is adsorbed on the surface of the rewarded voluminous Fe(III)-hydroxide.

Previous fundamental and applied research enabled pyrite, chalcopyrite, and arsenopyrite to be further used for various purposes, either in the form of finely divided particles or in the form of crystals:

- generation of pure hydrogen from aqueous pyrite slurries by electrolysis [27],
- a thermal battery cathode material [28],
- a photoactive material for photoelectrochemical and photovoltaic solar cells [29],
- a good electrocatalyst for oxygen reduction [30],
- 'carrier' for efficient copper ions removal from wastewater [31].
- sensors of ion-selective electrodes applied for different purposes (acid-base, precipitate, and redox investigations) in aqueous and non-aqueous solutions [6-10,32-36], Figure 1.

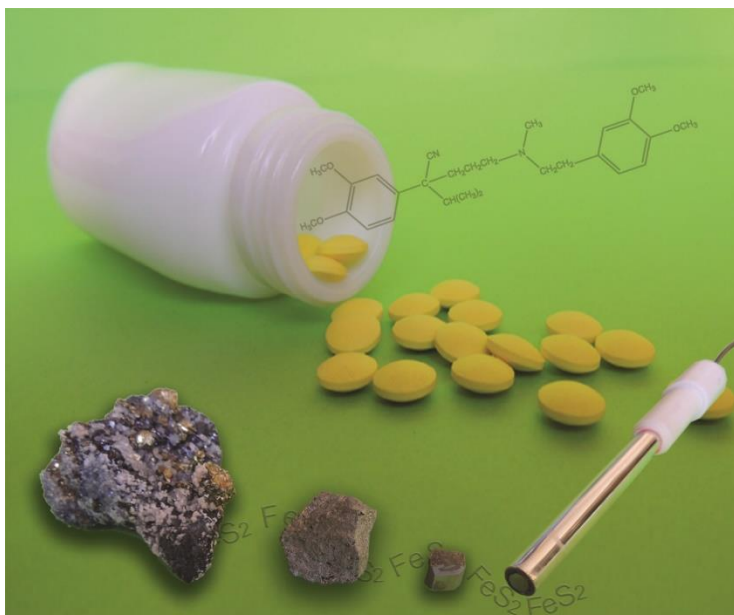
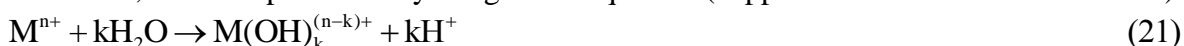


Figure 1. From natural mineral to laboratory-made electrode for different purposes.

3.2. Relationship between mineral surface properties and electrode potentials

Summarily observing the oxidation processes in the studied minerals, it can be concluded that in all cases products consist mainly of elemental sulfur, sulfates, Fe(II)-ions, Fe(III)-ions, Cu(II)-ions, various forms of Fe(III)-hydroxide, or Cu(II)-hydroxide. Hydrolysis of copper ions, as well as hydrolysis of iron, can be represented by the general equation (copper and iron are labeled with M):



Taking into account the hydrolysis process, as well as that pyrite, chalcopyrite, and arsenopyrite minerals manifest semiconducting properties, the system $M(OH)_k^{(n-k)+} / MIN$ behaves as a hydroxysulfide/metallic electrode (MIN stands for FeS_2 or $CuFeS_2$ or $AsFeS$). The potential of the solid-state membrane electrode without the internal solution (made by using pyrite, chalcopyrite or arsenopyrite as sensor materials), the external reference electrode, and the liquid junction between the sample solution and the external reference electrode labeled by using E_{ISE} , E_{ref} , and E_j , respectively, can be given by:

$$E = E_{ISE} - E_{ref} + E_j \quad (22)$$

If E_j is approximately constant, E can be expressed by:

$$E = L + S \log a_{ox} a_{H^+}^k \quad (23)$$

where L is a constant which depends on the construction of the membrane, S is a coefficient depending on the change of the potential of the ion-selective electrode caused by a variation of the activity of the H^+ ion, and $ox = M(OH)_k^{(n-k)+} / MIN$. Since during hydrolysis a solid layer is formed along the mineral surface itself, Equation 23 can be simplified and presented in this way:

$$E = L + S \log a_{H^+}^k \quad (24)$$

Based on the above equation, it can be concluded that the potential of electrodes made from these sulfide minerals depends on the activity of hydrogen ions.

Generally observed, if the electrode with a solid membrane (without internal solution) is sensitive to ion **A**, and the activity of ion **A** in the sample is equal to a_A , the membrane potential can be expressed as:

$$E = L + S \log a_A \quad (25)$$

In the case that the electrode is sensitive to ion **A** and some other ion **B**, then the potential can be represented by using the next equation [37]:

$$E = L + S \log \left(a_A + \sum_{B \neq A} K_{A,B}^{\text{pot}} a_B \right) \quad (26)$$

where $K_{A,B}^{\text{pot}}$ is the selectivity coefficient and if it is much less than 1, the electrode is much more sensitive to ion **A** than to ion **B**.

3.3. Electroanalytical characteristics of pyrite-, chalcopyrite- and arsenopyrite-based electrodes

The field of application, way of use, and service life of an electrode mainly depend on the sensor material and its properties. Therefore, great importance is attached to the sensors that exhibit certain ion-selectivity or universality, satisfactory mechanical resistance, and chemical inertness to the environment in which they are applied along with the ability to quickly establish an equilibrium potential. Although various types of electrodes have been developed for application in aqueous solutions, most of them are not applicable in non-aqueous solutions, because either their sensing membrane or supporting body is unstable in organic solvents.

Table 2. Electroanalytical performance of pyrite and chalcopyrite electrodes in water-acetonitrile mixture (1:9, v/v) (adapted from ref. [6]).

Parameter	Pyrite	Chalcopyrite
Slope (mV/decade)	48.0 ± 0.3	41.6 ± 0.5
Sensitivity (mV/decade cm^2)	192.0	166.4
Correlation coefficient	0.9974	0.9991
Linear range (mol/L)	$1.0 \times 10^{-5} - 1.0 \times 10^{-7}$	$1.0 \times 10^{-2} - 1.0 \times 10^{-4}$
Quantification limit (mol/L)*	3.2×10^{-7}	3.0×10^{-4}
Detection limit (mol/L)*	9.7×10^{-8}	8.9×10^{-5}
Response time (s)	12	13

*average of seven measurements (Cu(II) ion is an analyte that corresponds with the presented data)

In our laboratory, extensive investigations of various types of solid state have been performed (pyrite, chalcopyrite, covellite, chalcocite, galena, arsenopyrite, magnetite). In this review, the behavior of the electrodes whose sensory materials are based on pyrite, chalcopyrite, and arsenopyrite natural minerals will be considered.

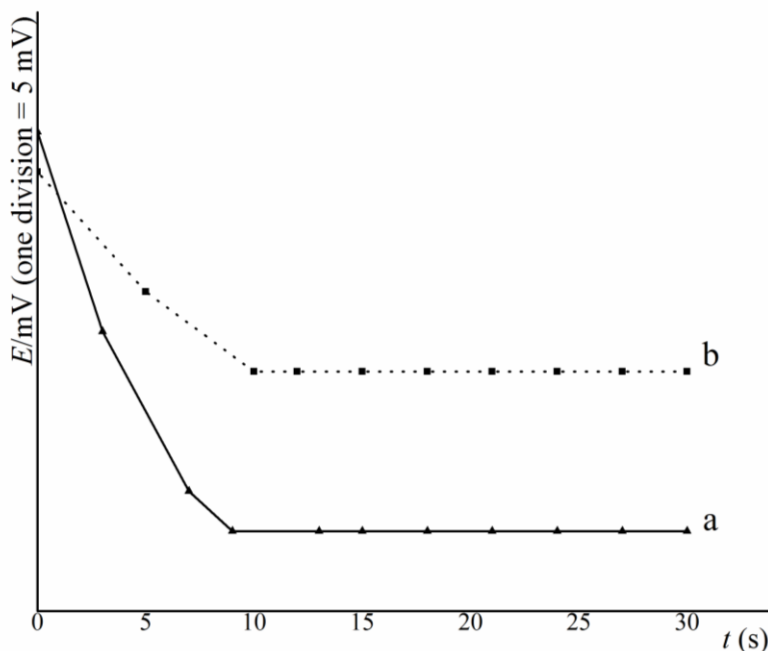


Figure 2. Plots of arsenopyrite electrode potential versus time in a) acetonitrile and b) propionitrile [9].

In order to use these electrodes for acid-base, precipitation, and redox determination in a non-aqueous environment, the sensor properties of these electrodes have been examined (a complete description of electrodes construction can be found in refs. 9 and 10). Some basic characteristics of the electrodes have been considered [6-10,32-37] and it can be concluded that pyrite, chalcopyrite, and arsenopyrite indicator electrodes possess very good predispositions (e.g., Figure 2 and Table 2) for their application for accurate determination of different substances, viewed over high potential stability, repeatability, sensitivity and selectivity, short-time response, wide linear concentration range, chemical inertness, and long-term chemical durability.

4. APPLICATION OF SENSORS

Ion-selective electrodes based on natural monocrystalline membranes have been developed and successfully used in studying various types of reactions and equilibria in non-aqueous solutions (Table 3).

Table 3. Application of pyrite, chalcopyrite, and arsenopyrite electrodes for determination of different compounds in various mediums*.

Electrode	Medium	Type of reaction	Substance determined	Ref.
FeS ₂	NM/EC, PN, AN, PN/EC	acid-base	<i>p</i> -toluensulphonic acid	[8,35]
			5-sulphosalicylic	[8,35]
			oxalic acid	[8,35]

	γ -BL, PC, PN/EC		trichloroacetic acid	[8,35]
			benzoic acid	[32,35]
			anthranilic acid	[32,35]
	γ -BL, PC		α -nitroso- β -naphthol	[32,35]
			salicylic acid	[32]
			3,4-dinitrobenzoic acid	[32]
			phthalic acid	[32]
			fumaric acid	[32]
			oxalic acid	[32]
	PN/EC		barbituric acid	[35]
			<i>N,N'</i> -diphenylguanidine	[35]
			arginine	[35]
			cysteine (hydrochloride)	[35]
			lizine	[35]
	Water/AN		<i>L</i> -ascorbic acid	[6]
	AN, PN	precipitation	hydroxylammonium chloride	[7]
			tetrabutylammonium bromide	[7]
			potassium iodide	[7]
			ammonium thiocyanate	[7]
			cetyltrimethylammonium bromide	[7]
			choline chloride	[7]
			verapamil hydrochloride	[7]
	AN, γ -BL, PC	redox	ferrocene	[10,34]
			tetrabutylammonium iodide	[10,34]
			thiourea	[10,34]
	AN		hydroquinone	[10]
	γ -BL, PC		phenylhydrazine	[34]
	Water/AN		<i>L</i> -ascorbic acid	[6]
CuFeS₂	NM/EC, PN, AN, PN/EC	acid-base	<i>p</i> -toluenesulphonic acid	[8,35]
			5-sulphosalicylic	[8,35]
			oxalic acid	[8,35]
			trichloroacetic acid	[8,35]
	γ -BL, PC, PN/EC		benzoic acid	[35,36]
			anthranilic acid	[35,36]
			α -nitroso- β -naphthol	[35,36]
	γ -BL, PC		salicylic acid	[36]
	PN/EC		barbituric acid	[35]
			<i>N,N'</i> -diphenylguanidine	[35]
			arginine	[35]
			cysteine (hydrochloride)	[35]
			lizine	[35]
	Water/AN		<i>L</i> -ascorbic acid	[6]
	AN, γ -BL, PC	redox	ferrocene	[10,34]
			tetrabutylammonium iodide	[10,34]
			thiourea	[10,34]
	AN		hydroquinone	[10]
	γ -BL, PC		phenylhydrazine	[34]
	Water/AN		<i>L</i> -ascorbic acid	[6]
FeAsS	AN, PN, γ -BL, PC	acid-base	benzoic acid	[9,33]

AN, PN	anthranlyic acid	[9,33]
	salicylic acid	[9,33]
	<i>N,N</i> -diphenylguanidine	[9]
	tributylamine	[9]
	collidine	[9]

*The amount of the respective compound lies the range 6-47 mg.
The standard deviation for all determinations is less than 1%.

The practical utility of the sensors has been tasted by their application as indicator electrodes for acid-base, precipitation, and redox titration in non-aqueous solvents (Sections 4.1 – 4.4). Recently, the natural minerals (pyrite and chalcopyrite) have been used as the working electrode for the detection and measurement of biologically important compound, hydrogen peroxide [38]. Compared with traditional non-enzyme biosensor that works in alkaline solution (Table 4) [39-45], the pyrite and chalcopyrite sensors can detect hydrogen peroxide even in acidic and neutral environment.

Table 4. Comparison between different H₂O₂ sensors.

Electrode material	Linear range (mol/L)	LOD (μmol/L)	Ref.
Modified GCE	$5.0 \times 10^{-4} - 1.0 \times 10^{-2}$	12.89	39
Modified GCE	$7.0 \times 10^{-5} - 3.0 \times 10^{-3}$	14	40
Modified GCE	$1.0 \times 10^{-7} - 5.0 \times 10^{-3}$	0.0025	41
GO-Ag	$1.0 \times 10^{-4} - 1.1 \times 10^{-3}$	28.3	42
Modified graphene	$1.0 \times 10^{-5} - 6.0 \times 10^{-4}$	10.1	43
Cu ₂ O/Au	$2.5 \times 10^{-7} - 5.0 \times 10^{-3}$	0.12	44
CuNWs	$5.0 \times 10^{-7} - 8.0 \times 10^{-4}$	0.4	45
FeS ₂	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	8.6	38
CuFeS ₂	$1.0 \times 10^{-4} - 3.0 \times 10^{-2}$	52	38

GCE – glassy carbon electrode, GO – graphene oxide, NWs – nanowires

4.1. Titration of acids and bases in different mediums

The most commonly used titrating agent in non-aqueous solutions (especially in PC and γ-BL) is the methanolic solution of potassium hydroxide and the next equilibria exist in this solution [36]:



In order to determine a weak organic acid (HA) in a non-aqueous solvent, for example, γ-butyrolactone, the acid should first be dissolved in the solvent:



During the titration process, lyonium ion reacts with methoxy anion (Equation 30), as represented in the following reactions:





For potentiometric titration in nitriles, tetrabutylammonium hydroxide, and sodium methylate are used in addition to potassium hydroxide in methanol. Tetrabutylammonium hydroxide behaves as the strongest base titrant in this environment. When comparative studies with a glass electrode are performed, tetrabutylammonium hydroxide shows benefit over potassium hydroxide because there is no harmful effect on the glass-electrode membrane during its use. Certainly, in the selection of titration agents, the properties of the reaction products play an important role, because the precipitate formed can interfere with the determination of titration end-point [36].

Titration acids/bases are of very similar concentration, so potential jumps at titration end-point directly depend on the dissociation constants of the acid/base, as well as the type of indicator electrodes. Additionally, the solvents have a significant influence on the height of the jump at the end-point, because they have direct leveling/differentiating effects on the acid/base strength (Table 5).

Table 5. a) Application of FeS_2 electrode for end-point detection in non-aqueous solutions [7,10,32,34].

Type of reaction	Titrated compound	Potential jumps, mV/0.3 mL			
		AN	PN	γ -BL	PC
Acid-base	benzoic acid	-	-	174	170
	anthranilic acid	-	-	187	164
	α -nitroso- β -naphthol	-	-	121	114
	salicylic acid	-	-	214	236
	3,4-dinitrobenzoic acid	-	-	91	89
	phthalic acid	-	-	103	101
	fumaric acid	-	-	83	81
	oxalic acid	-	-	182	178
Precipitation	hydroxylammonium chloride	141	169	-	-
	tetrabutylammonium bromide	260	270	-	-
	potassium iodide	192	194	-	-
	ammonium thiocyanate	132	138	-	-
	cetyltrimethylammonium bromide	284	281	-	-
	choline chloride	206	256	-	-
	verapamil hydrochloride	204	226	-	-
Redox	ferrocene	479	-	387	374
	tetrabutylammonium iodide	241	-	79	93
	thiourea	438	-	229	249
	hydroquinone	187	-	-	-
	phenylhydrazine	-	-	134	142

b) Potential jumps (mV/0.3 mL) at the end-point in the acid-base titration in γ -butyrolactone and propylene carbonate using pyrite, chalcopyrite, and arsenopyrite indicator electrodes [32,33,36].

Electrode	Titrated compound	Potential jump/ γ -butyrolactone	Potential jump/ propylene carbonate
FeS_2	benzoic acid	174	170

	anthranlyic acid	187	164
	α -nitroso- β -naphthol	121	114
	salicylic acid	214	236
	3,4-dinitrobenzoic acid	91	89
	phthalic acid	103	101
	fumaric acid	83	81
	oxalic acid	182	178
CuFeS₂	benzoic acid	115	114
	anthranlyic acid	83	86
	α -nitroso- β -naphthol	62	68
	salicylic acid	165	174
FeAsS	benzoic acid	150	120
	anthranlyic acid	125	106
	salicylic acid	197	186

Pyrite, chalcopyrite, and arsenopyrite ion-selective electrodes can be applied as sensitive sensors for determination of weak organic acids and bases in non-aqueous media, meeting the requirement for the presence of small amount of water in the non-aqueous solvents (Figure 3). If the amount of water is larger than 5% (v/v), the potential jump at the equivalence point is significantly reduced in all applied non-aqueous reaction environments [9,35,36].

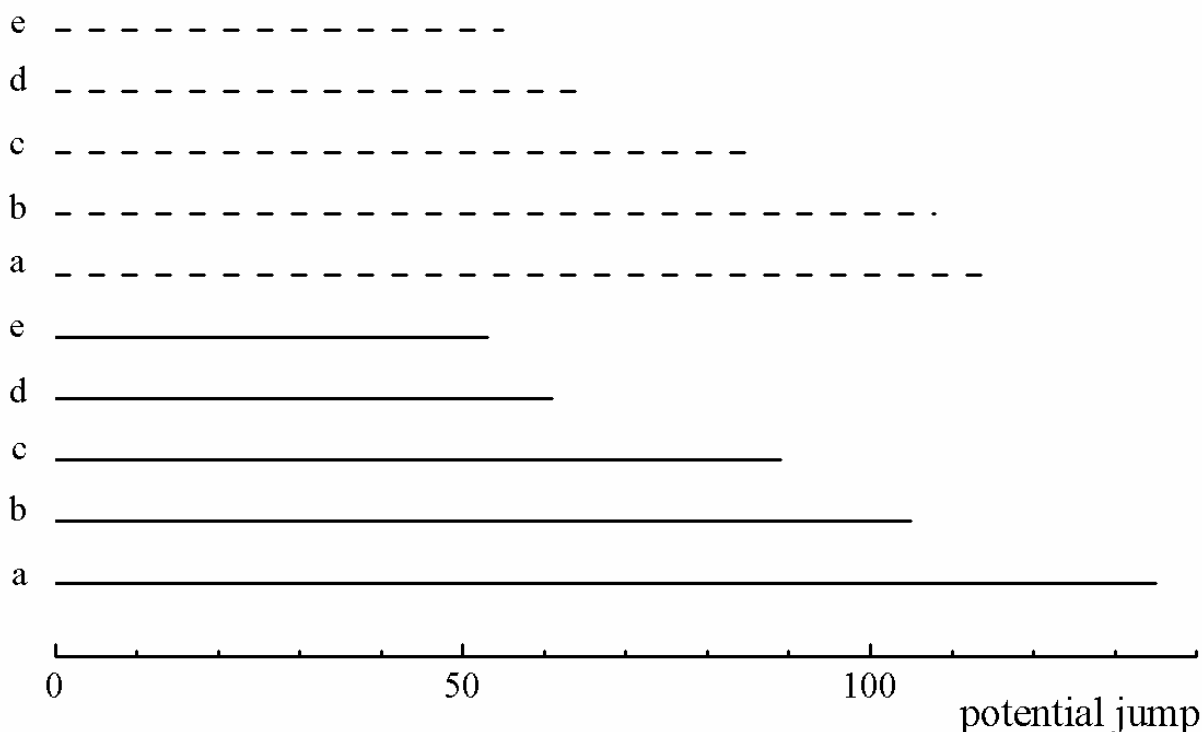


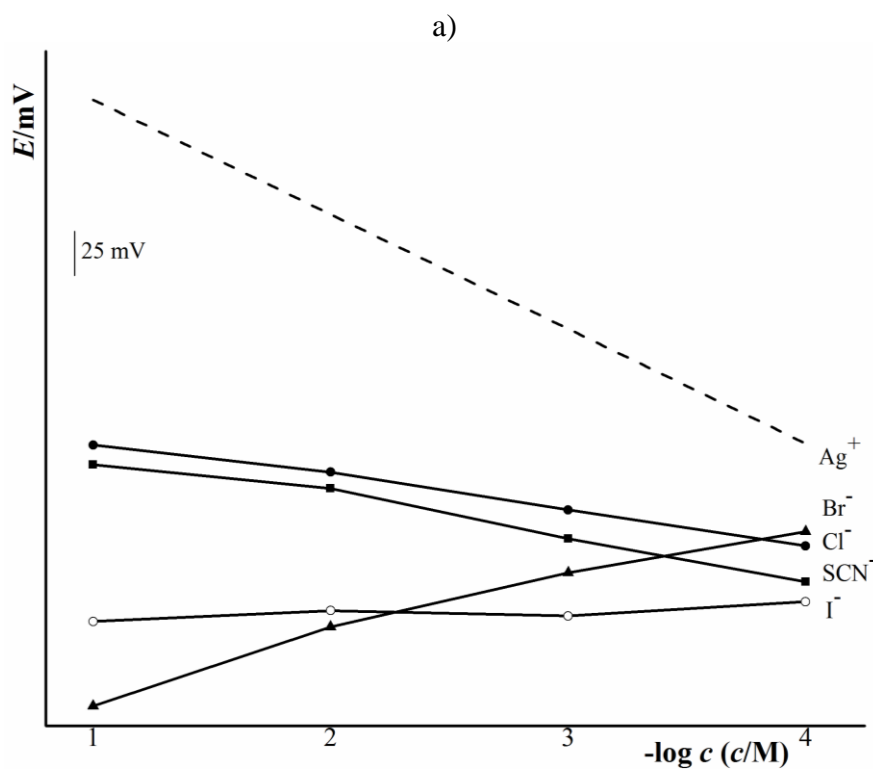
Figure 3. Effects of different water concentrations in γ -butyrolactone (—) and propylene carbonate (---) on potential jumps at the equivalence point in potentiometric titration of benzoic acid applying chalcopyrite as an indicator electrode: a) 0.0%, b) 0.5%, c) 1.0%, d) 5.0% and e) 10.0% of added water [36].

Evidently, the impact of water on the decrease of the potential is much more dramatic in the titration of very weak acids/bases.

4.2. Precipitation titrations

Although silver electrode is the most frequently used indicator electrode for argentometric precipitation titrations, there is evidence of the adsorption of halide anions onto the silver electrode in aqueous solutions [7,46,47]. The presence of specifically adsorbed anions can significantly influence the electrochemical reactivity of a metal electrode. It has also been demonstrated that non-aqueous solvents have a key role in this adsorption phenomenon.

Potentiometric technique combined with pyrite indicator electrode was found to be practically very useful in argentometric precipitation titrations of choline chloride, verapamil hydrochloride, and cetyltrimethylammonium bromide, including some conventional substances such as hydroxylammonium chloride, potassium iodide, tetrabutylammonium bromide, and ammonium thiocyanate in acetonitrile and propionitrile media [7]. Also, the pyrite-based sensor is highly selective to silver (Figure 4) over a number of examined ions.



b)

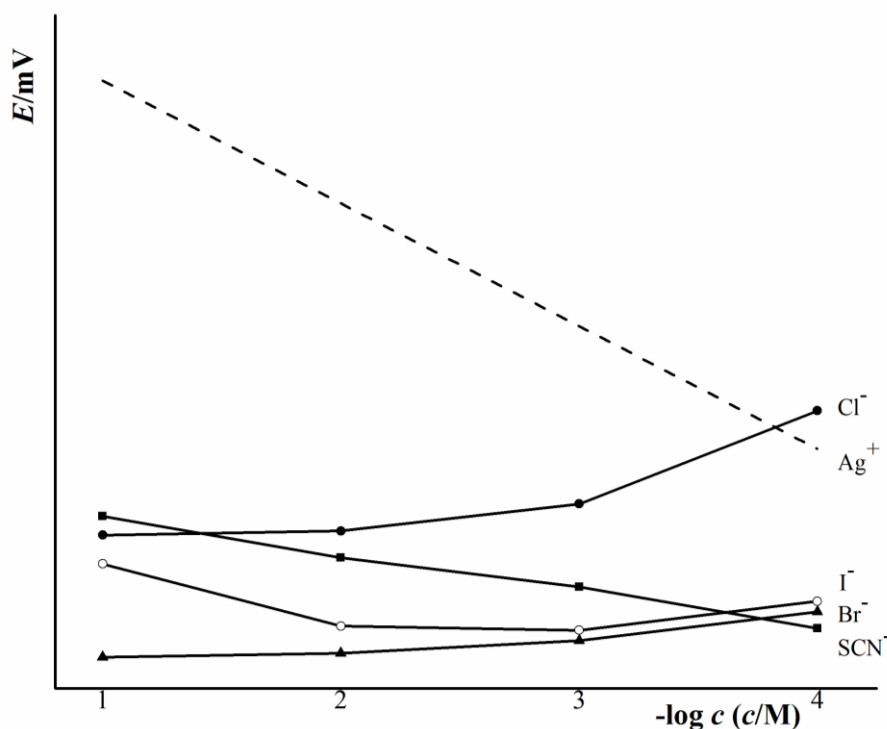


Figure 4. Potential response of pyrite electrode for different ions in a) acetonitrile and b) propionitrile [7] – Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

4.3. Redox titration

The main limiting factor for implementation of organic solvents as media for redox determinations is the stability of titrants in this environment [10]. One of the few that can be used as titrant is copper(II). Because of the strong solvation of Cu^+ in acetonitrile, for example, the standard potential of $\text{Cu}^{2+}/\text{Cu}^+$ couple in acetonitrile is much more positive than it could be expected from the donor number of acetonitrile. Thus, Cu^{2+} in acetonitrile is a strong oxidizing agent and it can be used in redox titration. Also, it is confirmed that copper(II) is a very suitable titrating agent in γ -butyrolactone and propylene carbonate [36].

The supporting electrolyte should be added to the electrolytic solution to make it electrically conductive and to eliminate the migration current (it flows in its absence). It has to be used in the concentration between 0.05 and 1.00 M, which is much higher than that of electroactive species.

As an indicator electrode for redox titration in both aqueous and non-aqueous media, Pt electrode is most commonly used. Our research has confirmed that pyrite, chalcopyrite, and arsenopyrite as sensors of indicator electrodes can be efficiently used for determination of different compounds (Tables 3 and 5). Some examples [10,34] and explanations are given below.

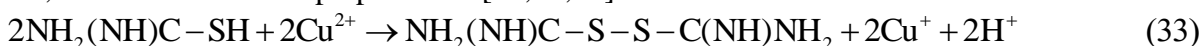
By the accidental discovery of ferrocene in the mid-20th century and due to its outstanding stability, intensive investigations of its potential in the field of drug development began. Ferrocene derivatives have been tested as drugs because of their unique properties such as non-toxicity and

stability under physiological conditions. Ferroquine, a ferrocene derivative, is today used as a commercial drug against malaria. Determination of ferrocene in different non-aqueous solvents leads to the conclusion that ferrocene is very stable in these media [10,34], as well as natural monocrystalline pyrite as an electrochemical sensor is very suitable for this purpose and it gives better results in potentiometric titration than commonly used Pt electrode:

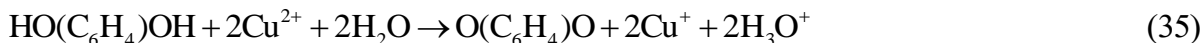


Ferrocene is oxidized rapidly and stoichiometrically to ferrocenium ion by using copper(II) in AN, PC and γ -BL.

Using pyrite and chalcopyrite indicator electrode and copper(II) as titrating agent, it is also possible to determine thiourea and iodide ion in organic solvents (Equations 33 and 34, respectively), which is of great interest because many drugs used to treat Graves' disease contain, among other substances, thiourea and iodide preparations [10,34,48]:



Hydroquinone, although known as a very effective bleaching agent in treating hyperpigmentation, has been withdrawn from use in many countries due to its harmful effects [49]. Owing to its carcinogenicity, genotoxicity, and toxicokinetic effects on human and its low degradation in the environment, it is considered a hazardous environmental pollutant [50]. It is possible to determine it by using sulfide minerals (Tables 3 and 5) and copper(II) as titrating agent:



In most cases, the presence of water is undesirable in titration in a non-aqueous environment. However, the presence of a small amount of water (around 0.2%) improves conditions for determination of hydroquinone (Figure 5). In this case (Equation 35), water has the role of a proton acceptor.

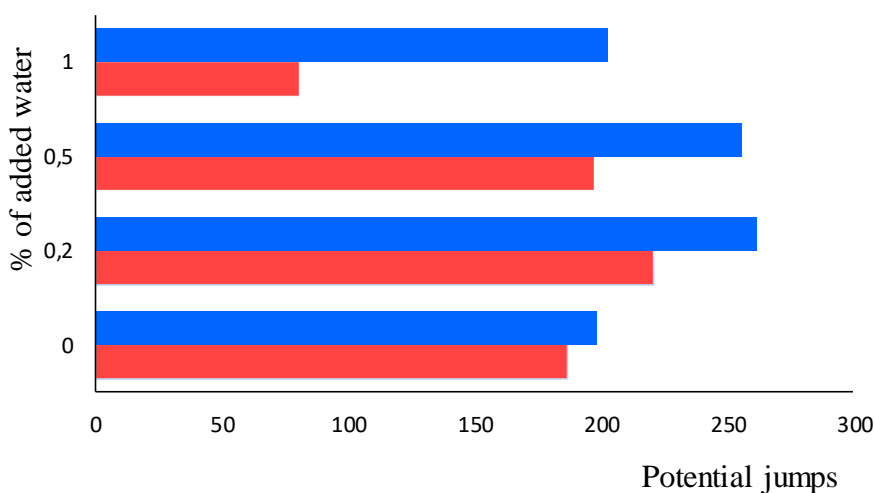


Figure 5. Usefulness of a small amount of water (increases the potential jump on the ETP) during hydroquinone determination in acetonitrile (FeS_2 – red and CuFeS_2 – blue color) [10].

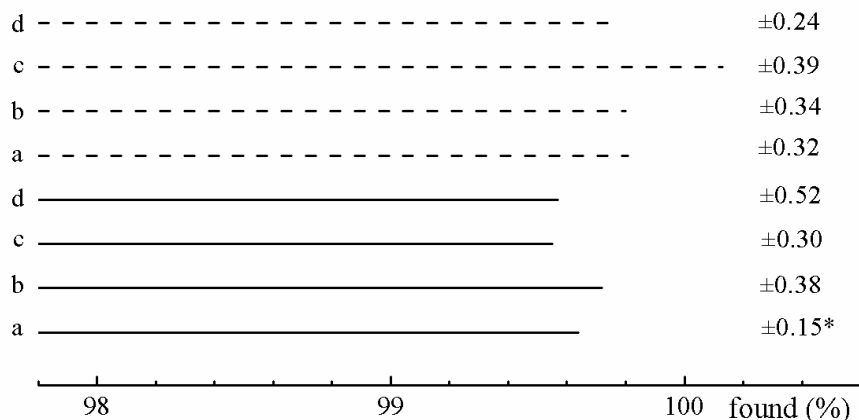


Figure 6. Results obtained in potentiometric titrations of different compounds in acetonitrile using pyrite (—) and chalcopyrite (---) electrodes: a) ferrocene, b) tetrabutylammonium iodide, c) thiourea and d) hydroquinone (*standard deviation of six measurements in %) [10].

The standard deviation of the results obtained in potentiometric titrations of ferrocene, thiourea, tetrabutylammonium iodide, and hydroquinone is less than 0.6% when pyrite and chalcopyrite electrodes are used (Figure 6).

L-Ascorbic acid, as an essential vitamin for the human body, is the subject of numerous investigations which include different techniques of its determinations [6]. In our laboratory, L-ascorbic acid is determined by using both acid-base and redox methods (Equation 36), as well as with pyrite and chalcopyrite electrodes.



In this case, the presence of non-aqueous solvent makes this reaction possible, as opposed to the occurrence in the aqueous environment. Therefore, the determination of the acid has been done in aqueous and in the mixture of water/non-aqueous solvent (1:9, v/v) with and without the presence of neocuproine [6]. Determination of an acid is not possible in aqueous solution in the absence of neocuproine, but the results of its determination in a non-aqueous solvent are excellent. Furthermore, it can be concluded that the results are twice as good for all indicator electrodes applied when an organic solvent is used as a medium in the presence of neocuproine [6].

4.4. Determination of different real samples in different mediums

Information gained from electrochemical measurements indicates that natural mineral pyrite, chalcopyrite, and arsenopyrite can be successfully applied for determination of many different compounds (Tables 3-5) [6-10,32-36], including some very important systems (verapamil, cetyltrimethylammonium bromide, choline chloride, ascorbic acid) and certain biologically active substances (cysteine hydrochloride, lysine, arginine, barbituric acid) [6,7,35]. Verapamil is a calcium channel blocker used in the management of angina, arrhythmia, and hypertension. Cetyltrimethylammonium bromide, a cationic surfactant, forms a multilayer film with DNA and the chemical structure of DNA is unchanged during this interaction, which makes this compound

applicable for biotechnological and biomedical investigations [51]. Choline, a precursor for biosynthesis, is used as a marker of cholinergic activity in the brain tissue in the clinical detection of Parkinson's and Alzheimer's diseases [52].

Table 6. a) Determination of *L*-ascorbic acid in pharmaceutical samples in water-acetonitrile mixture (1:9, v/v) (adapted from ref. [6]).

Sample	Found \pm RSD, %			Potential jumps, mV/0.3 mL		
	FeS ₂	CuFeS ₂	Pt*	FeS ₂	CuFeS ₂	Pt*
<i>Absence of a neocuproine</i>						
Vitamin C tablets	98.6 \pm 0.4	98.4 \pm 0.6	101.1 \pm 0.1	340	324	217
Vc injection	98.7 \pm 0.9	98.4 \pm 0.1	101.1 \pm 0.1	383	359	280
Multivitamin capsules**	98.5 \pm 0.6	101.6 \pm 0.2	98.7 \pm 0.3	336	342	301
<i>Presence of a neocuproine</i>						
Vitamin C tablets	98.6 \pm 0.4	98.2 \pm 0.6	101.1 \pm 0.2	594	437	364
Vc injection	98.9 \pm 0.9	98.8 \pm 0.8	98.3 \pm 0.1	546	512	391
Multivitamin capsules**	98.5 \pm 0.1	101.8 \pm 0.2	101.9 \pm 0.6	459	543	434

* reference method

** other components: vitamin E, vitamin A, sodium selenite

b) Analytical data obtained by using different electrodes for the determination of ascorbic acid [6,53-57].

Electrode	(Found \pm RSD, %)				Ref.
	Vitamin C tablet	Vitamin C effervescent tablets	Vitamin C ampoule	Multivitamine syrup	
Modified CPE	-	96.1 \pm 0.3	99.8 \pm 0.5	99.7 \pm 0.6	[53]
GCE	95.6 \pm 0.6	-	-	-	[54]
Modified GCE	-	101.1 \pm 2.1 (Merck) 93.4 \pm 2.9 (Bayer)	-	-	[55]
Modified GCE	96.3 \pm 0.7	99.9 \pm 0.1	99.6 \pm 0.3	-	[56]
Modified SPE	102.5 \pm 2.8	98.3 \pm 2.7	97.0 \pm 2.2	-	[57]
FeS ₂	98.6 \pm 0.4	-	98.7 \pm 0.9	98.5 \pm 0.6	[6]
CuFeS ₂	98.4 \pm 0.6	-	98.4 \pm 0.1	101.6 \pm 0.2	[6]

CPE – carbon paste electrode, SPE – screen printed electrode

In Table 6 are given some examples for determination of ascorbic acid. Summarily observed, the results for all discussed natural minerals were found to be deviating by less than 1%. The degree of accuracy of the other above-mentioned electrodes (CPE, GCE, SPE) is confirmed by the values obtained for the degree recovery, which ranged between 96.1 and 102.5%.

5. CONCLUSION

Water has a high permittivity and a wide range of working potential. However, solvents with poorly expressed acidic or basic properties often show a much wider scale of working potential in relation to water. This is why aprotic solvents, both protophilic and protophobic, are used in various ways in modern chemistry. Although water is an excellent and common solvent due to its ability to make hydrogen bond, it is difficult to dissolve large molecules and ions in it, unless they have hydrophilic ends in their structure. Accordingly, water is not suitable as a medium in reactions with large hydrophobic molecules and ions. On the contrary, molecules of most aprotic solvents do not interact between themselves, or they interact to a lesser degree, thus enabling the above-mentioned substances to be well-dissolved. This is why dipolar aprotic solvents are often used instead of water.

Non-aqueous solvents and new sensor materials have significantly expanded the field of applicability of the potentiometric method, increased selectivity, and sensitivity, as well as the number of substances that can be quantified. Electrodes based on sulfide minerals (pyrite, chalcopyrite, and arsenopyrite) with the rapid establishment of the equilibrium potentials and reproducible responses over a wide concentration range have exhibited chemical inertness and mechanical resistance in working mediums (γ -butyrolactone, ethylene carbonate, propylene carbonate, acetonitrile, propionitrile). No changes could be noticed on the electrodes during the application, so they can be used for unlimited time. Due to the simple construction, ease of handling, utilization without pretreatment or conditioning steps, possibility of successive application in various non-aqueous solvents, and taking into account the results obtained and average deviations and high accuracy and precision, it can be concluded that the electrodes can be successfully applied in organic solvents for acid-base, precipitation, and redox determination of various important compounds.

Information gained from electrochemical measurements indicates that pyrite, chalcopyrite, and arsenopyrite natural minerals used as electroactive materials are selected as the sensors that combine simplicity, efficiency, and reliability with low investment and maintenance costs. Additionally, they have good characteristics in terms of their applicability in non-aqueous media for the potentiometric determination of weak organic acid/bases, as well as biologically active compounds and some substances hazardous to the living environment. In this respect, this analytical technique is employed in many fields, including clinical and environmental analysis, physiology, and routine quality control analysis, providing accurate, prompt, and often selective determination of various chemical species.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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