# Natural monocrystalline chalcopyrite and galena as electrochemical sensors in non-aqueous solvents. Part II: potentiometric titrations of weak acids in *N,N*-dimethyformamide and *N*-methylpyrrolidone

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**Abstract** Natural monocrystalline chalcopyrite and galena as new indicator electrodes for the potentiometric titration of weak acids in *N,N*-dimethylformamide and *N*-methylpyrrolidone were used. The investigated electrodes showed a linear dynamic response for *p*-toluenesulfonic acid concentrations in the range from 0.1 to 0.001 M, with a Nernstian slope of 59.0 mV for chalcopyrite and 33 mV per decade for galena in *N,N*-dimethylformamide, 56.1 mV for chalcopyrite, and 32.0 mV per decade for galena in *N*-methylpyrrolidone. The potential in the course of the titration and at the titration end point was rapidly established. Sodium methylate, potassium hydroxide, and tetrabutylammonium hydroxide proved to be very suitable titrating agents for these titrations. The response time was less than 10–11 s, and the lifetime of the electrodes is limitless. The advantages of the electrodes are log-term stability, fast response, reproducibility, easy preparation, and low cost. The results obtained in the determination of the investigated weak acids deviated on average by ±0.04–0.34% from those obtained with a glass electrode.

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## Introduction

Titration in non-aqueous solvents has been traditionally an important tool for the accurate determination of various pharmaceuticals [1–4], the analysis of industrial process streams, the analysis of polymers [3], etc. Among non-aqueous solvents, *N,N*-dimethylformamide and *N*-methylpyrrolidone have often been used as the medium in numerous investigations.

*N,N*-Dimethylformamide (DMF) is a dipolar aprotic solvent with average ionizing properties, good dissociating power, and relative permittivity of 36.7 [5].

DMF was used as the medium for titrations with sodium methylate cyclic nitramines with visual and potentiometric determination of the titration end point using a glass electrode as the indicator [6], for the titration of substituted phenols with Azo Violet as the indicator [7], for the titration of thiacetazone and *iso*-niazide [8], and for the titration of certain salts as acids [9]. DMF was used as medium for the titration of phenols, carboxylic acid and phenolic acids [10–13], and fulvic acid with the use of an internal reference compound [14, 15], and as a solvent for determination of phenolic groups in lignin [16], the dissociation constant of 2,6-dinitro-4-chlorophenol; the dissociation constant carboxylic acids; the p$K_a$ values of certain sulfonamides [17–19] and some antioxidants [20]; the dissociation constants of 13 monosubstituted benzoic acids [21] and series of indicators [22, 23]; and the dissociation and homoconjugation constant of some acids and bases [24]. Robert Braun

used polarography, cyclic voltammetry, and controlled-potential coulometry to study a solution of nitrate in $N,N$-dimethylformamide [25].

*N*-Methyl-2-pyrrolidone (NMP) is a dipolar aprotic solvent. It has a relative permittivity of 32.2 [5], as well as a wide range of acidity ($pK_s$=24.3). It has been used in analytical practice since 1970, thanks to the papers by Gaplern et al. [26]. Although NMP is a more basic solvent than water, it has a high relative permittivity; it dissolves numerous organic and inorganic compounds, as well as showing a sufficient differentiation capacity. In the literature, there are not many papers on its analytical application. Korenman and Yermolaeva used DMP for the titration of phenols [27] and alkylphenols [28], while Galpern et al. used it for the titrations of both phenols and weak organic acids in mixtures [26].

As can be seen from the literature data, $N,N$-dimethylformamide and methylpyrrolidone are extensively used as the medium in potentiometric determinations of many acidic substances. A glass electrode was most frequently used as the indicator electrode, both in aqueous and non-aqueous media. In an aqueous environment, glass electrodes are very popular due to their high selectivity and dynamic pH range. However, in spite of the distinctive potential characteristic of pH-glass electrodes and their use in routine pH measurements for many years, they have certain limitation, such as high resistance, brittleness, instability in hydrofluoric acids, and fluoride-containing media, difficulties of miniaturization and contamination of the membrane. In addition, a large deviation from Nernstian behavior is observed when a glass electrode is used in extreme acidic and basic conditions. In solutions of high alkalinity, the $H_3O^+$ ions in the gel layer of a glass electrode can be substituted partially or totally by other cations, usually $Na^+$ and $K^+$ ions [29], leading the electrode to respond to these metal cations (alkaline error). On the other hand, in high acid concentrations, the gel layer of a glass electrode suffers a decrease in the number of adsorbed water molecules, which affects the hydrogen ion activity on its surface, leading to an acidic error [30]. In non-aqueous media, these electrodes show certain undesirable features: The potential response of a glass electrode in non-aqueous solution is often very slow.

The development of alternative electrodes for pH measurement and potentiometic titrations (both in water and in non-aqueous medium) is of considerable interest in the sense of eliminating some of the presented limitations of a glass electrode (high resistance, brittleness, contamination of the membrane, alkaline error, and dehydration of the glass membrane in non-aqueous media). In previous papers, many deficiencies of the glass electrode were eliminated by the use of natural monocrystalline pyrite as the electrochemical sensor for the potentiometric titration of

weak acids in pyrrolidone, $N,N$-dimethylformamide, and pyridine [31], and the employment a chalcopyrite and galena in $\gamma$-butyrolactone and propylene carbonate [32]. Since $N,N$-dimethylformamide and $N$-methylpyrrolidone are very useful solvents, they have been extensively used as the medium in potentiometric determinations of many acidic substances. Therefore, in this study, the possibility of the application of chalcopyrite and galena as electrochemical sensors for potentiometric titrations of weak acids in these solvents was investigated.

## Experimental

### Reagents

All the chemicals used in the present study were of analytical reagent grade from Merck, Fluka, or Baker.

*N,N*-Dimethylformamide and *N*-methylpyrrolidone were puriss p.a. purity: $N,N$-dimethylformamide (≥99,8%) with a water content of ≤0.1% and methylpyrrolidone (≥99%) with a water content of ≤0.1%. These solvent were used without further purification. The water content in the applied solvents was checked by Karl Fischer titration.

Solutions of acids ($\alpha$-nitroso-$\beta$-naphthol, benzoic acid, and stearic acid) were prepared by dissolving a weighed amount of an acid in the titration solvent. The concentration of the acid solutions were controlled by titration with standard 0.1 M Bu$_4$NOH (tetrabutylammonium hydroxide) using visual end-point detection or potentiometric end-point detection by means of a glass electrode-modified saturated calomel electrode (SCE) couple.

*p*-Toluenesulfonic acid monohydrate was dried in vacuo over $P_2O_5$ at 70–80 °C for several days.

A solution of sodium methylate in a mixture of benzene and methanol was prepared as follows: about 6 g of sodium was washed with methanol and then immediately dissolved in 100 ml of methanol. The solution was protected from carbon dioxide while the sodium was dissolving; if necessary, the solution was cooled in cold water to prevent the reaction from becoming too violent. When all of the sodium had reacted, 150 ml of methanol and 1,500 ml of benzene were added and the reagent stored in borosilicate glassware protected from carbon dioxide. The concentration of the final solution was determined by titration against benzoic acid dissolved in benzene-methanol. Although the reagent is reasonably stable, it should be restandardized every few days.

Tetrabutylammonium hydroxide (laboratory-reagent grade) 0.1 M in 2-propanol-methanol (10:1 *v/v*; Fluka) was standardized against benzoic acid with Thymol Blue as the indicator.

The Thymol Blue solution was prepared by dissolving 0.1 g of Thymol Blue in 100 ml of methanol.

Potassium hydroxide (laboratory-reagent grade) 0.1 M in ethanol (Riedel-de Haën) was standardized against benzoic acid with Thymol Blue as the indicator.

The required volume of the acid solution was measured by means of a micro-burette with a PTEF stopcock; 2.00 ml of the investigated acids were measured.

All measurements were performed at room temperatures between 20 and 25 °C.

## Electrodes

The indicator chalcopyrite and galena electrode has been described in a previous paper [32, 33].

The response of the indicator chalcopyrite and galena electrode in N,N-dimethylformamide and N-methylpyrrolidone was compared with that of a conventional glass electrode type G-202C (Radiometer, Copenhagen). The glass electrode was conditioned in the appropriate solvent before used.

The experiments were performed with either a sample of natural chalcopyrite or a galena crystal from the Veliki Krivelj copper mine (Bor, Serbia) and the Stari Trg lead mine (K. Mitrovica, Serbia).

The reference electrode was a modified SCE containing methanolic potassium chloride solution. The solution was vigorously stirred with a magnetic stirrer during the titration.

## Apparatus

The apparatus used to follow the potential changes of the chalcopyrite and galena electrode with time and for end-point detection with a chalcopyrite–SCE, galena–SCE, or a glass electrode–SCE couple was described in a previous paper [32]. The potential changes during the titration were followed with a Digital 870 pH-meter, Dresden.

The same apparatus with an additional temperature-controlled cell was used to follow the potential changes of the employed electrode as a function of the concentration of p-toluenesulfonic acid.

## Procedure

### Potential measurement

Stationary potential measurements of the chalcopyrite and galena electrode were performed in a series of p-toluenesulfonic acid solutions in the concentration range of 0.1–0.001 M. The potential of these electrodes with time was followed in a temperature-controlled cell (25±0.1 °C). The ionic strength of the solution was maintained at 0.05 M with tetrabutylammonium perchlorate. The potential values determined in this way were used for the calculations of the slopes.

The change of the potential of the chalcopyrite and galena electrodes with time was followed in the required solvent. These indicator electrodes were coupled with a modified SCE as the reference electrode.

### Potentiometric titration

A certain volume (15 ml) of the required solvent, which had previously been titrated, was placed in the titration vessel, and a measured volume of the to-be-investigated acid and two drops of the indicator solution were added. The indicator electrode, either the chalcopyrite or galena, or glass electrode and a modified calomel electrode as the reference were immersed in the solution and connected to a pH meter. The solution was then titrated potentiometrically by adding 0.05 or 0.1 ml aliquots of 0.1 M tetrabutyl-ammonium hydroxide (potassium hydroxide or sodium methoxide), and the potential was read after each addition of the titrant. The potential measurements were made at 2-min intervals during the course of the titration. The titration end-points were determined by the classical method from the second derivative.

## Results and discussion

### Mechanism

Chalcopyrite [$CuFeS_2$] is the most abundant copper-bearing mineral in the world [34]. The resistivity of chalcopyrite ranges between $150–9,000×10^{-6}$ $\Omega$m [35], and the Néel temperature is 659 °C [34]. Stable $\alpha$-chalcopyrite undergoes a transformation to a cubic form ($\beta$-chalcopyrite) accompanied by a minor loss of sulfur (<1%) at 550 °C [34]. This phase is isostructural with sphalerite. The system is complex, with bornite ($Cu_5FeS_4$) and talnakhite ($Cu_9Fe_8S_{16}$) appearing at intermediate transition temperatures [34].

The oxidation state of the cations in chalcopyrite was a subject of debate for some time, although spectroscopic studies indicate that copper is present in the copper (I) formal oxidation state [36, 37], while iron is present in the high-spin ferric state [38]. There is an absence of a magnetic moment on the copper atom observed in neutron diffraction experiments, but the iron moment is anomalously low ($3.82\mu_B$), which has led to proposals of an oxidation state intermediate between $Fe^{2+}$ and $Fe^{3+}$ [38].

The non-oxidative solubility of chalcopyrite in water is low: $2.35×10^{-6}$ M at 100 °C [34]. In the presence of acid, the reaction is slow and can be expressed as follows:

$$CuFeS_2 + 2H^+ \rightleftarrows CuS + 2Fe^{2+} + H_2S \qquad (1)$$
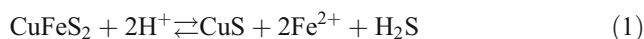
It is more intensely dissolved only in the presence of stronger oxidizing agents giving rise to different oxidation

products [$Cu^{2+}$, $Cu^+$, $Fe^{3+}$, $Fe^{2+}$, $S^o$, $SO_4^{2-}$, $Cu(OH)^+$, $Fe(OH)^{2+}$, $Fe(OH)_3$, etc.], which depend on many factor (the nature of the oxidant, pH value, temperature, nature and concentration of the cations present, anions and other chemical species, etc). In dump and heap leaching, chalcopyrite is oxidized by Fe(III) ions or dissolved oxygen in sulfuric acid solution to release Cu(II) and Fe(II) ions [39, 40].

Sulfur, sulfate, and the cations $Cu^{2+}$, $Fe^{2+}$, and $Fe^{3+}$ are obtained using anode oxidation of chalcopyrite. As is known, the hydrolysis of the cations is favored by increasing the pH of the solution; iron cations are hydrolyzed at lower pH values than copper ones, and therefore, only hydrolysis of iron cations will be considered in the further text [32]. By hydrolysis of $Fe^{3+}$ ions, hydroxide is formed on the surface of the chalcopyrite electrode.

Since chalcopyrite is known to be a semiconductor, the system $Fe(OH)_k^{(n-k)+}/CuFeS_2$ behaves as a hydroxysulfide/metallic electrode; its potential is defined by:

$$E = E_{ox}^o + \frac{RT}{nF} \ln a_{ox} a_{H_3O^+}^k \qquad (2)$$

where $ox = Fe(OH)_k^{(n-k)+}\Big/CuFeS_2$

If hydrolysis leads to the formation of solid particles in the vicinity of the chalcopyrite surface, the equation for the potential of the chalcopyrite electrode can be simplified:

$$E = E_{ox}^o + \frac{RT}{nF} \ln a_{H_3O^+}^k \qquad (3)$$

From Eq. 3, it follows that the potential of the chalcopyrite electrode depends on the activity of the $H_3O^+$ particles. Equation 3 can also be applied to non-aqueous solutions containing weak organic acids.

Galena is the natural mineral form of lead sulfide. Surface oxidation of galena has been the subject of countless studies. Interest in the oxidation of galena surface has been stimulated by different areas of its application. For example, lead sulfide has been used as a material for infrared detectors and semi-transparent glasses, and investigated as a possible material in solar energy cells. However, most of the studies dealing with the problem of PbS oxidation have been related to flotation, by which galena is separated from gangue and other minerals. It is now well accepted that galena is oxidized through an electrochemical corrosion mechanism with reduction of oxygen as the cathodic process. Nevertheless, there is no agreement regarding the mechanism of the anodic oxidation. In particular, the following three reactions, which are thermodynamically probable, have all been suggested as possible initial steps of the anodic decomposition of galena:

I. Formation of a metastable sulfur-rich/metal-deficient sulfide under-layer (or elemental sulfur), yielding $Pb(OH)_2$ [41] in alkaline solutions.

II. At pH 7–10, direct formation of sulfur and a lead hydroxide monolayer through reaction with water [42–44].

III. A congruent dissolution–oxidation [45–48] that is followed by hydrolysis of the released ions and anodic oxidation of the hydrolyzed sulfur anion to elemental sulfur ($HS^- \rightleftarrows S^o + H^+ + 2e^-$ at pH 9.2). Along with the formation of lead hydroxide, lead thiosulfate [49] or anions of thiosulfate are formed [48].

As can be seen from literature data, the electrochemical behavior of galena is similar to that of chalcopyrite. The potential of a galena electrode in aqueous solution is defined by:

$$E = E_{ox}^o \frac{RT}{nF} + \ln a_{H_3O^+}^k \qquad (4)$$

where $ox = Pb(OH)_2/PbS$

From Eq. 4, it follows that the potential of the galena electrode depends on the activity of the $H_3O^+$ particles. Equation 4 can also be applied to non-aqueous solutions containing weak organic acids.

## Characteristics of a chalcopyrite and galena ISE electrode

If an ISE electrode is to be applied as a sensor for quantitative measurements in a non-aqueous environment, the following conditions should be fulfilled: stable potential in acid and base medium, sufficient slope, short response time, and long lifetime.

### Potential of the chalcopyrite and the galena electrode

The stationary potentials of the chalcopyrite and of the galena electrode in N,N-dimethylformamide and N-methylpyrrolidone were measured by direct potentiometry at 25±0.1 °C in a freshly prepared 0.05 M solution of p-toluenesulfonic acid in the appropriate solvent. All measurements were performed in the presence of a background electrolyte of constant ionic strength (0.05 M tetrabutylammonium perchlorate) in order to minimize the effect of streaming and diffusion potentials in the streaming sample solution. In all the investigated solutions, a stable potential was attained in less than 4–5 min.

### Slope of the potential response of the chalcopyrite and the galena electrode

The potential of chalcopyrite and galena electrodes was read using a series of p-toluenesulfonic acid solutions in the concentration range 0.1–0.001 M in a temperature-controlled cell (25±0.1 °C). The ionic strength of the solutions was maintained with 0.05 M tetrabutylammonium

perchlorate. The values of the slope of the potential in a *N,N*-dimethylformamide was 59.0 mV for chalcopyrite and 33 mV for galena (Figs. 1 and 2). Similar slopes were obtained for *N*-methylpyrrolidone (56.1 mV for chalcopyrite and 32.0 mV per decade for galena). Since the chalcopyrite and the galena electrodes exhibit sub-Nernst dependences, they cannot be used for the measurement of the pH of the solutions. However, since the potential of a chalcopyrite and a galena electrode as an indicator electrode is very stable with respect to time, they can be successfully applied to the titration of acids in *N,N*-dimethylformamide and *N*-methylpyrrolidone as the solvent.

*Response time of the electrodes*

The response time of the chalcopyrite and galena electrode was determined by recording the time elapsed before a stable potential value was attained after immersion of the chalcopyrite, i.e., galena electrode, and the reference electrode (modified SCE) were into calibration solutions ranging from highly acidic (0.05 M of *p*-toluenesulfonic acid) to highly basic (0.05 M tetra-*n*-butylammonium hydroxide or 0.05 M KOH) solutions. The change of the electrode potential for the chalcopyrite electrode when going from the acidic (*p*-toluenesulfonic acid) to the basic region (TBAH) ranged from +219 to −194 mV (*N*-methylpyrrolidone) and from +204 to −199 mV (*N,N*-dimethylformamide), and for the galena electrode when going from the acidic (*p*-toluenesulfonic acid) to the basic region (KOH) ranged from +113 to −140 mV (*N*-methylpyrrolidone). The response time for chalcopyrite electrode was 10 s and for galena electrode 11 s in both solvents. These results are within the limit of the results obtained by many hydrogen electrodes giving a linear response within the same pH range. In conclusion, the
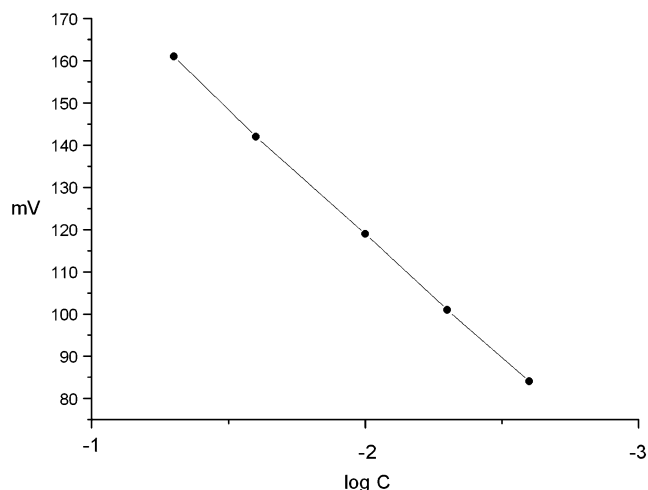


**Fig. 1** Plots of the chalcopyrite electrode potential vs. log c (*p*-toluenesulfonic acid) in *N,N*-dimethylformamide
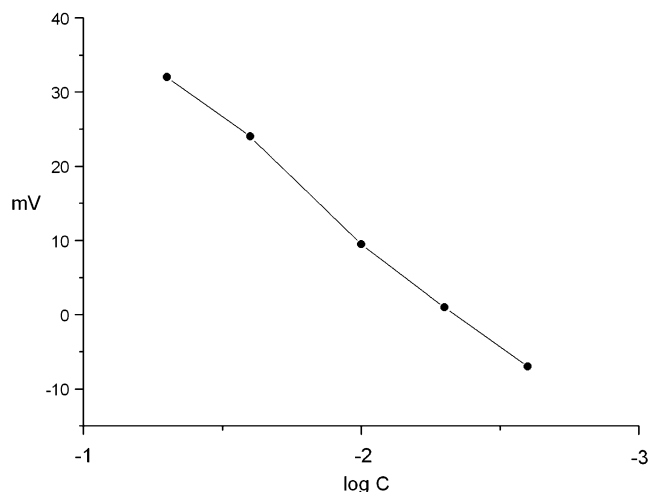


**Fig. 2** Plots of the galena electrode potential vs. log c (*p*-toluenesulfonic acid) in *N,N*-dimethylformamide

response times of the prepared chalcopyrite and galena electrodes were compatible with most similar electrodes reported in the literature [50, 51].

*Lifetime of the electrodes*

The lifetimes of the electrodes were determined by raising the potential values of the calibration solution (*p*-toluenesulfonic acid) and plotting the calibration curves for a period of 1 year. The slope of the electrodes remained the same. However, if the electrode was used frequently and for a long time, it was necessary to rub the crystal chalcopyrite and galena with aluminum oxide and wash the electrode before continuing use.
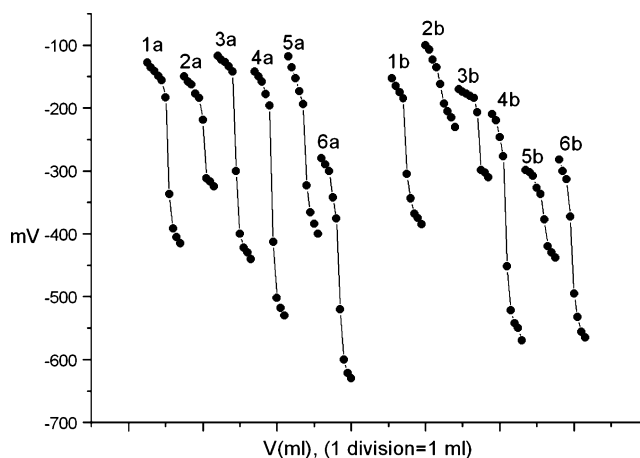


**Fig. 3** The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid (**a**) and α-nitroso-β-naphthol (**b**) in methylpyrrolidone: *1a*, *3a*, *5a*, *1b*, *3b*, and *5b* chalcopyrite electrode; *2a*, *4a*, *6a*, *2b*, *4b*, and *6b* glass electrode. Titrant: *1a*, *2a*, *1b*, and *2b* sodium methylate; *3a*, *4a*, *3b*, and *4b* KOH; *5a*, *6a*, *5b*, and *6b* TBAH
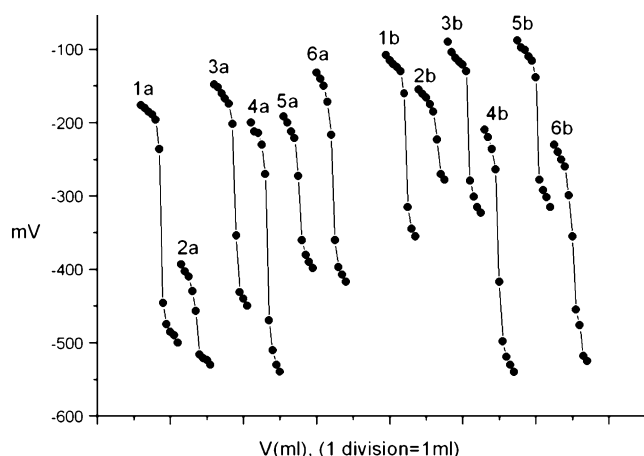
**Fig. 4** The effect of the indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid (**a**) and $\alpha$-nitroso-$\beta$-naphthol (**b**) in *N,N*-dimethylformamide: *1a*, *3a*, *5a*, *1b*, *3b*, and *5b* chalcopyrite electrode; *2a*, *4a*, *6a*, *2b*, *4b*, and *6b* glass electrode. Titrant: *1a*, *2a*, *1b*, and *2b* sodium methylate; *3a*, *4a*, *3b*, and *4b* KOH; *5a*, *6a*, *5b*, and *6b* TBAH

(a)   Analytical application

*Titration of acids in N,N-dimethylformamide and N-methylpyrrolidone*

Tetrabutylammonium hydroxide, potassium hydroxide, and sodium methylate are most frequently used as the titration medium for the titration of acidic substances in *N,N*-dimethylformamide and *N*-methylpyrrolidone as solvent with a glass electrode as the indicator electrode. Due to the alkaline error of a glass electrode [29], they are less frequently used as a base titrant, as base titration means that they contain sodium or potassium ions in their

molecules (sodium methylate, KOH). Since in this study the new sensors chalcopyrite and galena are proposed instead of a glass electrode in the determination of the titration end point (TEP), in addition to TBAH, sodium methylate and KOH in anhydrous methanol were used as the titration means in all the present experiments.

The practical utility of the proposed sensor was tested by its use as an indicator electrode for the titration of weak acids of different strengths, such as benzoic, stearic, and $\alpha$-nitroso-$\beta$-naphthol, with methanolic potassium hydroxide, TBAH, and sodium methylate solution.

The neutralization reactions of acids in non-aqueous solvent with TBAH, KOH, and sodium-methylate were presented in our previous papers [31, 32].

The titration curves of benzoic acid and $\alpha$-nitroso-$\beta$-naphthol in *N*-methylpyrrolidone as the solvent with sodium methylate, potassium hydroxide, and TBAH as titrant using the electrode couples chalcopyrite–SCE and glass–SCE are shown in Fig. 3. The titration curves of benzoic acid and $\alpha$-nitroso-$\beta$-naphthol in *N,N*-dimethylformamide with sodium methylate, potassium hydroxide, and TBAH as titrant using the electrode couples chalcopyrite–SCE and glass–SCE are shown in Fig. 4. While titrating benzoic acid, for example, the potential jumps at the TEP were 263 mV/ 0.3 ml in *N,N*-dimethylformamide and 237 mV/0.3 ml in *N*-methylpyrrolidone when a chalcopyrite electrode was employed as the sensor and sodium methylate as the titrant. When benzoic acid was titrated using the same sensor with KOH in the same solvent, the potential jumps were 265 mV/ 0.3 ml in *N,N*-dimethylformamide and 250 mV/0.3 ml in *N*-methylpyrrolidone. In the titration of benzoic acid using a glass electrode as the indicator, the potential jumps at the titration end point (TEP) with KOH as the titrant were about 300 mV/0.3 ml in both *N*-methylpyrrolidone and *N,N*-

**Table 1** Potential jumps (mV/0.3 ml) at the end-point in the potentiometric titration of acids in *N,N*-dimethylformamide and pyrrolidone

| Solvent | Titrated acid | Titrating agent | CuFeS$_2$–SCE | PbS–SCE | Glass–SCE |
|---|---|---|---|---|---|
| *N,N*-Dimethylformamide | Benzoic acid | Sodium methylate | 263 | 120 | 91 |
| | Benzoic acid | Potassium hydroxide | 265 | 128 | 310 |
| | $\alpha$-Nitroso-naphthol | Sodium methylate | 215 | 110 | 86 |
| | $\alpha$-Nitroso-naphthol | Potassium hydroxide | 200 | 123 | 262 |
| | $\alpha$-Nitroso-naphthol | TBAH[a] | 182 | 56 | 219 |
| | Stearic acid | Sodium methylate | 279 | 110 | |
| | Stearic acid | Potassium hydroxide | 257 | 141 | 284 |
| | Stearic acid | TBAH | 159 | 49 | 225 |
| Pyrrolidone | Benzoic acid | Sodium methylate | 237 | 118 | 124 |
| | Benzoic acid | Potassium hydroxide | 250 | 125 | 331 |
| | Benzoic acid | TBAH | 193 | 48 | |
| | $\alpha$-Nitroso-naphthol | Sodium methylate | 183 | 103 | 60 |
| | $\alpha$-Nitroso-naphthol | Potassium hydroxide | 119 | 98 | 231 |
| | $\alpha$-Nitroso-naphthol | TBAH | 109 | 46 | 219 |

[a] New sensor
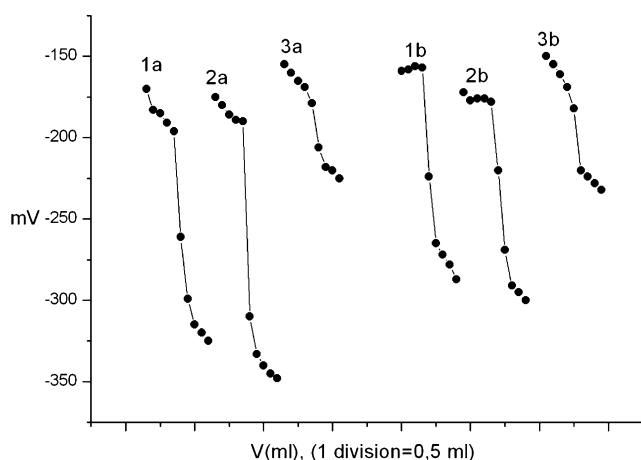
**Fig. 5** The effect of the galena indicator electrode on the shape of the end-point inflexion in the potentiometric titration of stearic acid (**a**) and α-nitroso-β-naphthol (**b**) in *N,N*-dimethylformamide. Titrant: *1a* and *1b* sodium methylate; *2a* and *2b* KOH; *3a* and *3b* TBAH

dimethylformamide (Table 1). When a glass electrode was used for TEP detection, the potential jumps were decreased (124 mV/0.3 ml in *N*-methylpyrrolidone and 91 mV/0.3 ml in *N,N*-dimethylformamide) and were hardly perceptible when sodium methylate was applied as the titrant, due to the effect of the sodium ions on the glass electrode.

While titrating α-nitroso-β-naphthol (weak acids, p$K_a$ in water of 7.77) with chalcopyrite as the sensor, high potential jumps were obtained in the titration with sodium methylate (183 mV/0.3 ml in *N*-methylpyrrolidone and 215 mV/0.3 ml in *N,N*-dimethylformamide). Sufficiently high potential jumps in *N*-methylpyrrolidone and *N,N*-dimethylformamide were obtained with the other two titrants as well (with KOH 119 mV/0.3 ml in *N*-methylpyrrolidone and 200 mV/0.3 ml in *N,N*-dimethylformamide, while with TBAH, 109 mV/

0.3 ml in *N*-methylpyrrolidone and 182 mV/0.3 ml in *N,N*-dimethylformamide).

When benzoic, stearic, and α-nitroso-β-naphthol are titrated with KOH and sodium methylate as the titrants in the same solvents and with galena as the sensor, nearly half-lower potential jumps on TEP are obtained. If the same acids are titrated with TBAH, the jumps are either very small or missing (Figs. 5 and 6).

When chalcopyrite is used as the sensor in potentiometric titrations with KOH as the titrant, the potential jumps on TEP *N,N*-dimethylformamide and *N*-methylpyrrolidone as solvents are twice higher than the potential jumps obtained using the same sensor in γ-butyrolactone and propylene carbonate [32] (265 mV/0.3 ml in *N,N*-dimethylformamide and 250 mV/0.3 ml in *N*-methylpyrrolidone, and 135 mV/0.3 in γ-butyrolactone and 114 mV/0.3 ml in propylene carbonate, respectively). Also, a pronounced difference in the potential jumps on TEP is obtained in the titration of weak acid α-nitroso-β-naphthol (200 mV/0.3 ml in *N,N*-dimethylformamide, 183 mV/0.3 in *N*-methylpyrrolidone, and only 62 mV/0.3 ml in γ-butyrolactone and 68 mV/0.3 ml in *N*-methylpyrrolidone). The obtained results are in accordance with physical–chemical properties of *N*-methylpyrrolidone and *N,N*-dimethylformamide: more basic than water, high relative permittivity, sufficient differentiation capacity, and a wide range of acidity. *N*-Methylpyrrolidone and *N,N*-dimethylformamide are suitable solvents for the titration of acids and γ-butyrolactone and propylene carbonate for the titration of bases. In addition, all three titrants (KOH, TBAH, and sodium methylate) can be applied in *N*-methylpyrrolidone and *N,N*-dimethylformamide for the titration of acids, while only KOH in γ-butyrolactone and propylene carbonate.
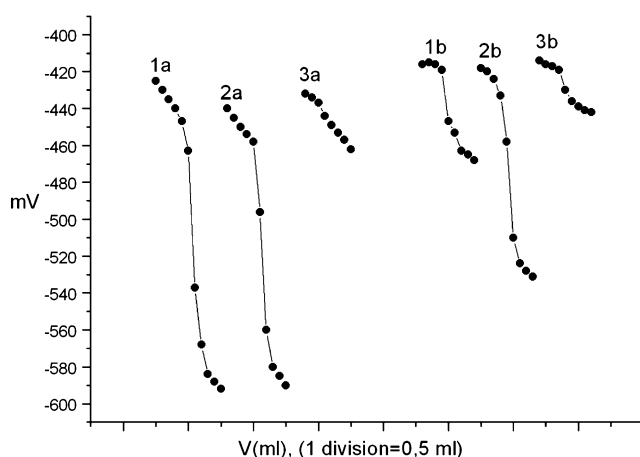


**Fig. 6** The effect of the galena indicator electrode on the shape of the end-point inflexion in the potentiometric titration of benzoic acid (**a**) and α-nitroso-β-naphthol (**b**) in methylpyrrolidone. Titrant: *1a* and *1b* sodium methylate; *2a* and *2b* KOH; *3a* and *3b* TBAH
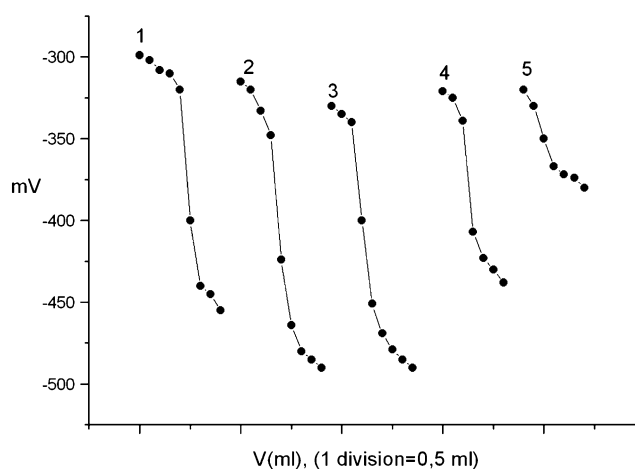


**Fig. 7** Potentiometric titration curves of α-nitroso-β-naphthol in *N*-methylpyrrolidone obtained by using a chalcopyrite as indicator electrode and TBAH as the titrant: *1* non-aqueous media, *2* 0.5%, *3* 1.0%, *4* 5.0%, and *5* 10.0% water in methylpyrrolidone

**Table 2** Potentiometric titration of weak acids in *N,N*-dimethylformamid and pyrrolidone by the application of the electrode pairs CuFeS2–SCE and glass–SCE

| Titrated acid | Solvent | No. of determinations | Taken (mg) | Found (%) | |
|---|---|---|---|---|---|
| | | | | Glass–SCE | CuFeS$_2$–SCE |
| Benzoic acid | *N*-Methylpyrrolidone | 7 | 21.20 | 99.80±0.10 | 99.95±0.32[a] |
| Benzoic acid | *N*-Methylpyrrolidone | 6 | 21.20 | 100.11±0.22 | 100.20±0.26[b] |
| Benzoic acid | *N*-Methylpyrrolidone | 5 | 21.20 | 99.78±0.30 | 99.85±0.30[c] |
| α-Nitroso-β-naphthol | *N*-Methylpyrrolidone | 6 | 57.27 | 98.78±0.32 | 98.90±0.51[a] |
| α-Nitroso-β-naphthol | *N*-Methylpyrrolidone | 7 | 57.27 | 97.47±0.24 | 97.55±0.45[b] |
| α-Nitroso-β-naphthol | *N*-Methylpyrrolidone | 6 | 57.27 | 98.60±0.20 | 98.30±0.40[c] |
| Benzoic acid | *N,N*-Dimethylformamide | 6 | 19.38 | 99.85±0.40 | 99.92±0.22[a] |
| Benzoic acid | *N,N*-Dimethylformamide | 6 | 19.38 | 99.86± 0.25 | 99.90±0.36[b] |
| α-Nitroso-β-naphthol | *N,N*-Dimethylformamide | 7 | 15.22 | 98.00±0.35 | 98.20±0.40[a] |
| α-Nitroso-β-naphthol | *N,N*-Dimethylformamide | 6 | 15.22 | 98.20±0.42 | 98.12±0.35[b] |
| α-Nitroso-β-naphthol | *N,N*-Dimethylformamide | 7 | 15.22 | 97.95± 0.31 | 98.28±0.30[c] |
| Stearic acid | *N,N*-Dimethylformamide | 5 | 42.70 | 97.85±0.27 | 97.60±0.20[a] |
| Stearic acid | *N,N*-Dimethylformamide | 6 | 42.70 | 97.66±0.11 | 97.80±0.13[b] |
| Stearic acid | *N,N*-Dimethylformamide | 6 | 42.70 | 97.70±0.25 | 97.85±0.21[c] |

[a] Sodium methylate

[b] Potassium hydroxide

[c] TBAH

When galena is used as the sensor for potentiometric titrations with KOH as the titration medium, the potential jumps on TEP in γ-butyrolactone and propylene carbonate are somewhat higher than in *N,N*-dimethylformamide and *N*-methylpyrrolidone.

The proposed electrodes cannot be applied in potentiometric titration in the solvents that dissolve crystal carrier. In these solvents, sensor carrier must be made of teflon or some other material that is not soluble in the investigated solvent.

When the chalcopyrite and galena electrodes were applied as indicator electrodes in *N,N*-dimethylformamide

and *N*-methylpyrrolidone as solvent, the potential during the titration and at the equivalence point (TEP) were rapidly established (within a few minutes) and the change of the potential at the TEP coincided with the change of the applied indicator color.

Water lowers the potential jumps at the TEP in all the applied solvents. α-Nitroso-β-naphthol titration curves in *N*-methylpyrrolidone with chalcopyrite as the sensor and TBAH as the titrant in the presence of different concentrations of water are shown in Fig. 7. If the solvent contained 0.5% water, the potential jump at the TEP was 129 mV/0.3 ml. If 1% or 5% water was present, the jumps

**Table 3** Potentiometric titration of weak acids in *N,N*-dimethylformamide and pyrrolidone by the application of the electrode pairs PbS–SCE and glass–SCE

| Titrated acid | Solvent | No. of determinations | Taken (mg) | Found (%) | |
|---|---|---|---|---|---|
| | | | | Glass–SCE | PbS–SCE |
| Benzoic acid | *N*-Methylpyrrolidone | 6 | 21.22 | 99.80±0.10 | 99.95±0.40[a] |
| Benzoic acid | *N*-Methylpyrrolidone | 6 | 21.22 | 100.11±0.22 | 100.20±0.30[b] |
| α-Nitroso-β-naphthol | *N*-Methylpyrrolidone | 5 | 57.27 | 98.78±0.32 | 98.80±0.50[a] |
| A-Nitroso-β-naphthol | *N*-Methylpyrrolidone | 7 | 57.27 | 97.47±0.24 | 97.60±0.45[b] |
| Benzoic acid | *N,N*-Dimethylformamide | 6 | 19.38 | 99.80±0.40 | 99.89±0.32[a] |
| Benzoic acid | *N,N*-Dimethylformamide | 6 | 19.38 | 99.82± 0.25 | 100.16±0.30[b] |
| A-Nitroso-β-naphthol | *N,N*-Dimethylformamide | 7 | 15.22 | 98.06±0.35 | 98.10±0.40[a] |
| A-Nitroso-β-naphthol | *N,N*-Dimethylformamide | 6 | 15.22 | 98.10±0.42 | 98.18±0.30[b] |
| Stearic acid | *N,N*-Dimethylformamide | 5 | 42.70 | 97.78±0.27 | 97.800±0.26[a] |
| Stearic acid | *N,N*-Dimethylformamide | 6 | 42.70 | 97.70±0.15 | 97.82±0.34[b] |

[a] Sodium methylate

[b] Potassium hydroxide

were 114 mV/0.3 ml and 107 mV/0.3 ml, respectively. If the solvent contained 10% water, there was no jump at the TEP. The impact of water on the decrease of the potential was much stronger in the titrations of very weak acids. Since water is released during the titration of acids when applying TBAH and KOH, it is best to use sodium methylate as the titrant in such cases.

The results obtained in the determination of investigated acids (Tables 2 and 3) in *N,N*-dimethylformamide and *N*-methylpyrrolidone as solvent, using a chalcopyrite and galena as indicator electrode, deviated on average by ±0.04–0.34% from those obtained with a glass electrode.

## Conclusion

The obtained results show that a natural monocrystalline chalcopyrite electrode can be successfully applied as an indicator electrode for the titration of weak acids in *N,N*-dimethylformamide and *N*-methylpyrrolidone, with standard base solutions (KOH, sodium methylate, and TBAH). If natural monocrystalline galena is used as a sensor, somewhat lower, but sufficient potential jumps on (TEP) are obtained using KOH and sodium methylate as titrants. The potential in the course of the titration and at the equivalence point (TEP) were found to be rapidly established. The investigated sensors are easy to prepare, low cost, of great hardiness and chemical inertness, and as working mediums, are very suitable for potentiometric titrations in the investigated solvents.

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