Potentiometric determination of nickel (II) with sodium diethyldithiocarbamate (NaDEDC)

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Abstract. The article presents the results of potentiometric titration of the solution containing Ni (II) by the solution of sodium diethyldithiocarbamate (NaDEDC). The possibilities of carbon composite electrode (CCE) and certain ion-selective and metal electrodes as the sensors for potentiometric determination of ions were investigated. The conditions for potentiometric titration of nickel (reagent, pH, composition of supporting solution, efficient electrode, effect of interfering ions) using sensors have been studied and optimized. The titration curves were processed by the linearization method which provide determination of equivalence point with high accuracy.

1. Introduction
Production of nickel is increasing every year due to rising rates of industry. Nickel has very valuable properties therefore this element is mostly used as an ingredient of steel and certain alloys, also it finds wide application in the production of catalysts, batteries and in the electrical engineering industry. Its products such as nickel-based catalysts have an important role in the reactions between organic compounds. However, nickel is well known as a toxic metal. Nickel control in different objects is performed by physical [1-5] and physicochemical [6-8] methods of analysis, many of which demand the expensive equipment, reagents and additional sample preparation step. Electrochemical methods of analysis are advantageous because of their polyfunctional performance, high accuracy, low cost and simplicity. The efficiency of an electrochemical method is determined by the use of appropriate detection system (i.e. indicating electrode or sensor). Therefore implementation of new electrode systems in the routine analysis is prospective area of analytical chemistry. Due to the urgent need for selective monitoring of nickel ions in many samples, it is necessary to improve potentiometric titration method and to develop new methods for compounds determining including the selection of an appropriate sensor for the potentiometric titration. Nickel ion selective electrode as a sensor for nickel ions determination is produced in industry, however, potentiometric titration method allows to expand the number of alternative working electrodes. One of the proposed electrode is a new electrochemical sensor, carbon composite electrode (CCE), which was previously shown to use in potentiometric determination of some heavy metals [9].
In this work the CCE, lead-, sulphide-, silver-ion selective electrodes (ISE), platinum and silver metal electrodes has been proposed as a sensors for the potentiometric titration of Ni (II). The conditions for the Ni (II) determination were studied and have been optimized.

2. Experimental part
The potentiometric measurements were performed with the pH meter/ionomer Ethan (Russia). The reference electrode was Ag/AgCl electrode. The new sensor CCE was made of polyethylene concentrate containing 30% carbon with uniform distribution of particles in the bulk of electrode [10]. Simulating solutions were prepared by dissolving in distilled water with subsequent serial dilution of Ni(NO₃)₂. Solution of NaDEDC was used as a titrant for providing sedimentary potentiometric titration. NaDEDC was added to analyt with a pneumatic microburette. The acidity of a solution was measured with pH-meter.

The potentiometric titration of Ni (II) and Cd (II) was performed according to the following procedure. The 0.5 ml portions of a titrant were added to the solution. Portions were reduced to 0.2 ml near the equivalence point. The electromotive force was recorded after each addition of a titrant portion and solution stirring until a stable potential is reached. All titration curves were transformed into a linearity by the fragmentary linear approximation method in order to determine the equivalence point. This method was developed by B. M. Marianov. Method helps to determine the equivalence point at any part of the titration curve. The principle of the method is to use the mathematical model to transform a titration curve into a linear regression [11].

2.1. The titrant for potentiometric titration of Ni (II)
Dithiocarbamates have gained widespread use in potentiometry among chelating agents for titrimetric determination of metal ions. NaDEDC in particular is widely used in analysis due to its reactivity, simple synthesis and other essential analytical properties.

It forms a low-soluble precipitate with Ni (II) ions in the ratio 1:2 in a wide pH range according to equation 1:

\[ \text{Ni}^{2+} + 2\text{DED}^- \rightarrow \text{Ni} \text{(DED)}_2 \downarrow \]  

(1)

The sensitivity of the CCE and metal electrodes toward DEDC⁻ ion may be explained by the redox properties of the titrant. The redox pair of oxidized and reductive forms of dithiocarbamate – thiuram disulfide reagent arises in NaDEDC solution (equation 2) and the indicator electrode exhibits its redox behaviour. In the case of ion selective electrodes sensitivity associated with formation of enduring complex compounds in a boundary layer of the electrode.

\[ 2\text{(C}_2\text{H}_5\text{)}_2\text{NCS–S}^- \rightleftharpoons (\text{C}_2\text{H}_5\text{)}_2\text{NS–S–SN(C}_2\text{H}_5\text{)}_2 \]  

(2)

2.2. The analytical response of Ni (II) on CCE, ISEs and metal electrodes
The typical potentiometric curve for Ni (II) with NaDEDC using CCE is shown in figure 1. Titration curves were transformed into a linear plot by the linearization method in order to determine the equivalence point. Since there are pronounced jumps on the titration curves, the AB regions were processed for this purpose.

Figure 1b shows the linear plot for AB region, which is approximated by a straight line with a good correlation coefficient \( r = 0.9999 \); the slope \( V_{eq} \) (Ni) is \( 3.964\pm0.001 \) mL. This demonstrates good agreement between the titration model and the experimental data. The precipitate solubility \( K_{sp} \) value of a precipitate formed has a sufficient impact on the results of potentiometric titration. The experimental solubility product of Ni(DED)₂ was calculated to be \( 1.5\times10^{-13} \) using a regression intercept term \( y_0 \).

The experimental data obtained with the CCE were compared with data obtained using a range of ISEs and metal indicating electrodes under the same conditions.

Figure 2 shows that all obtained by titration of 25 mL \( 6\times10^{-4} \) M Ni (II) with \( 3\times10^{-3} \) M NaDEDC titration curves are sufficiently informative excepting curve received with silver metal electrode. The
curves with the most pronounced jump in potential were obtained with CCE and platinum metal electrode. The CCE advantage is polyfunctionality and it has a lower cost and better performance.

**Figure 1.** a – Potentiometric titration curve for the simulation solution of $6 \times 10^{-4}$ M Ni (II) with $3 \times 10^{-3}$ M NaDEDC using CCE; the aliquot volume is 25 ml; b – the linear plot for AB fragment of the titration curve.

**Figure 2.** Jumps in potential values of titration curves using indicating electrodes:
1 – lead-ISE;
2 – platinum metal electrode;
3 – silver-ISE;
4 – sulphide-ISE;
5 – CCE;
6 – silver metal electrode.

2.3. Effect of supporting Electrolyte on Ni (II) titration
Supporting electrolytes and buffer solutions were used in order to stabilize the ionic strength and to keep pH constant for better reproducibility of analysis results. It is especially necessary to add the supporting electrolyte to very dilute solutions with low conductivity in order to reach a stable electrode potential.

A decrease of the jump in potential is observed for Ni (II), with the pH increase up to 8 in ammonia buffer solution and pH lower than 3. It is impossible to conduct the potentiometric titration in strong acidic solutions because of the decomposition of NaDEDC (low-soluble diethylidithiocarbamic acid is formed) and in alkaline medium due to hydrolysis. Also determination is worsening with borax buffer because the metal forms complex compounds with buffer ions. The curves with the most pronounced jumps in potential were obtained at the pH range from 3 to 7 using acetate buffer solution and KNO$_3$.
supporting electrolyte. The solution of KNO₃ can stabilize the ionic strength and prevent the Ni (II) surface adsorption.

2.4. Effect of Interfering Ions
The NaDEDC titrant can also interact with other metal ions to form stable coordination complexes. As a result, metal ions can affect the potentiometric determination of Ni (II) when they are in a titration solution. The stability of some complex ions of a metal with NaDEDC is as follows [12]:

\[
\text{Hg(II)} > \text{Pd(II)} > \text{Ag(I)} > \text{Cu(II)} > \text{Bi(III)} > \text{Co(II)} > \text{Pt(II)} > \text{Cd(II)} > \text{Ti(II)} > \text{Zn(II)} > \text{In(III)} > \text{Sb(III)} > \text{Fe(III)} > \text{Te(IV)} > \text{Mn(II)}.
\]

The degree of proceeding of a titration reaction [13] can be a useful criterion to estimate the possibility of the separate determination of Ni (II) in a two-component solution containing one of the mentioned interfering ions. It shows which part (in %) of analyt has reacted with the titrant by the time the interfering ion starts to react with it.

The degree of proceeding is aimed to define the possibility of separate identification of ions in a solution. The value calculated to be 100% indicating the total conversion of ion separately from the interfering ion by receiving titration curve with two separate jumps of potential. At a value 99.8% and below it is thus possible to conduct determination obtaining summary jump in potential corresponding to titration of ions together. The larger the difference between the \( K_s \) values enables more likely to achieve separate determination.

For the titration of mixture Cd-Ni, the degree of proceeding at a point of inflection in a titration curve was calculated to be 74.88% indicating impossibility of performance the total conversion of Cd (II) separately from the interfering ion.

2.5. Potentiometric titration of Cd (II)
NaDEDC forms a low-soluble precipitate with Cd (II) ions in the ratio 1:2 according to equation 3:

\[
\text{Cd}^{2+} + 2\text{DEDC}^- \rightarrow \text{Cd(DEDC)}_2
\] (3)

The typical potentiometric curve for Cd (II) with NaDEDC using CCE has descending appearance. The titration curves were transformed into a linear plot by the linearization method in order to determine the equivalence point. The linear plot is approximated by a straight line with a good correlation coefficient \( r = 0.9996 \); the slope \( V_{eq} \ (\text{Cd}) \) is 8.09±0.29 mL. This also demonstrates a good agreement between the titration model and the experimental data. The experimental solubility product of Cd(DEDSC)_2 was calculated to be \( 8.42\times10^{-12} \) using a regression intercept term \( y_0 \).

Cadmium can be titrated exclusively in acidic medium. The curves with the most pronounced jump in potential were obtained at the pH range from 3 to 4 using tartrate and acetate buffer solutions.

2.6. Simulation solutions of Ni (II) and Cd (II)
The interfering effect of Ni (II) can be eliminated by adding a masking agent. To perform separate determination of Ni (II) and Cd (II) it was suggested to use dimethylglyoxime (DMG) as an additive component. DMG was chosen based on its bonding properties to Ni (II) ions expressed in a formation of complex more enduring (\( K_s=\text{Ni(C}_2\text{H}_4\text{O}_2\text{N}_2)_2=2.3\times10^{-25} \)) than complex obtained with NaDEDC.

Figure 4 shows the titration curve of solution containing Ni (II) and Cd (II) with total jump in potential. The jump corresponds to titration of Cd (II), since Ni (II) ions do not react with NaDEDC due to formation of nickel complex compound with DMG, hence under these circumstances separate determination of Cd (II) ions becomes possible.
Figure 3. Potentiometric titration curves of 25 ml solution containing $1\times10^{-3}$ M of Nickel (II) with $9\times10^{-3}$ M NaDEDC using CCE in acetate buffer; 1 – without addition of DMG, 2 – with an addition of DMG.

Figure 4. Potentiometric titration curve of 25 ml solution containing $1\times10^{-3}$ M of Ni (I) and $2\times10^{-3}$ M Cd (II) with 0.01 M NaDEDC using CCE in acetate buffer.

3. Summary
The conditions for Ni (II) potentiometric titration in working solutions have been optimized and the procedure for Ni (II) determination by potentiometric precipitation titration with NaDEDC as a titrant has been developed. The conditions of differentiated determination of nickel and cadmium ions from a single solution by potentiometric titration with computer processing results of fragmentary linearization method were studied. Relative standard deviation for the Ni (II) and Cd (II) determination was typical for potentiometric titration analysis.

References
[1] Saçmacı Ş and Saçmacı M 2017 A new procedure for determination of nickel in some fake jewelry and cosmetics samples after dispersive liquid–liquid microextraction by FAAS Appl Organometal Chem. 31
[2] Dohnalova L, Bucek P, Vobornik P and Dohnal V 2017 Determination of nickel in hydrogenated fats and selected chocolate bars in Czech Republic Food Chemistry Feb 217 456-60
[3] Liu Nana 2018 Determination of Nickel, Cobalt and Manganese in cathode material of Lithium ion Batteries International Journal of Electrochemical Science 13
[4] Xi, H, Liu, Q and Chen Z 2018 Determination of nickel (II) at nanomolar levels using iodide-responsive gold-copper nanoparticles as colorimetric probes Microchim Acta 185 88
[5] Khudhair Ahmed Fadhil 2018 A Simple Pre-concentration Method for the Determination of Nickel (II) in Urine Samples Using UV-Vis Spectrophotometry and Flame Atomic Absorption Spectrometry Techniques Indonesian Journal of Chemistry 19
[6] Sharma Harish 2014 Potentiometric Determination of Nickel (II) Ion Using Zirconium (IV) Antimono Tungstate as an Electroactive Material American Chemical Science Journal 4 457-71
[7] Sharma Harish Kumar, Dogra Pernita, Gupta Akhilesh Kumar, and Koohyar Fardad 2014
[8] Potentiometric determination of Nickel (II) ion using 2-hydroxy-1-naphthylidene-N-cyanoacetohydrazone as electroactive material Quimica Nova 37(8) 1324-8
[9] Punrat E, Tutiyasarn P, Chuanuwatanakul S and Chailapakul O 2017 Determination of nickel (II) by ion-transfer to hydroxide medium using sequential injection-electrochemical analysis (SIECA) Talanta 168 286-90
[10] E A Kuzminskaya, S V Shumar 2015 Explore the use of solid composite electrode for the potentiometric determination of heavy metals in Multifunctional Chemical Materials and
Technologies 2015 Conference Proceedings edited by Yu G Slizhov (Tomsk State University Tomsk Russia 3 226–8

[11] G N Noskova 2012 Solid carbon containing composite electrodes for voltammetric element determination Ph.D thesis Tomsk Polytechnic University

[12] B M Marianov, A G Zarubin, S V Shumar 2003 J. Anal. Chem. 58(4) 342–6

[13] V M Byrko 1984 Dithiocarbamates Nauka Moscow (in Russian) 342 p

[14] V K Chebotarev 1998 Talanta 47 1043–51