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Usefulness of the voltamperometric method for assessment of the purity of soil

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Abstract

This paper presents a voltammetric analysis of soil. It shows that the voltammetry is a useful method for the assessment of soil contaminated with heavy metal ions. There are two major problems with voltammetry analysis: the diffusion coefficient and the measurement system. The paper contains a short literature study of mathematical equations and a study of differences between soil and water measurements. Suggestions of the solution of these problems and the results obtained by the author are also presented.

Keywords: soil, voltammetry, heavy metals.

Przydatność metody woltamperometrii stałoprądowej do oceny czystości gleb

Streszczenie

Artykuł przedstawia możliwości zastosowania metody woltamperometrycznej do badania stopnia zanieczyszczenia gleb metalami ciężkimi. Wstępne, wykonane przez autorkę pomiary, pozwalają stwierdzić, że metody elektrochemiczne mogą być użyteczne do oceny stopnia zanieczyszczenia gleb metalami ciężkimi. Metody elektrochemiczne są dobrze poznane i powszechnie wykorzystywane w pomiarach roztworów wodnych. Różnice między pomiarami w roztworach wodnych a pozostałych wydają się być na tyle znaczne, że mogą wykluczać metody elektrochemiczne jako metody pomiarowe użyteczne dla pomiarów glebowych. Ważne jest rozwiązanie problemów wynikających z tych różnic. Główne problemy uniemożliwiające użycie metod elektrochemicznych najprawdopodobniej wynikają z różnic w wartości współczynnika dyfuzji i czułości układu mierzacego (związana z konstrukcją samego układu) dla pomiarów glebowych oraz w wodzie. W niniejszym artykule zostało przedstawione zarówno krótkie studium literaturowe, propozycja rozwiązania problemów występujących podczas pomiarów, jak i własne wyniki badań autorki.

Słowa kluczowe: woltamperometria, gleba, metale ciężkie.

1. Introduction

Nowadays, as a result of increased input from industry, traffic and agriculture, the soil contamination is one of the biggest problems. The pollution of soil by heavy metals ions can be measured by several methods, e.g. spectrometry or electrochemistry ones. One of them, is a ion selective sensor. The ion selective sensor allows for measurement the concentration of an individual ion. The spectrometry allows measuring more than one, but this method is expensive and destroys the soil samples [4] [8]. Therefore there is a need to find a cheap, quick and non-invasive method. A voltammetry can be a solution for problems with heavy metal ion in soil measurements.

2. Theoretical fundamentals of voltammetry

Voltammetry is a very useful and well known electrochemistry method which is used for measurements of reduction/oxidation solutions. The measured current is a function of the applied potential. A three electrode measurement system is used in voltammetry measurements (Fig. 1) [1, 4, 5].

The area of working electrode *WE* should be 50 times larger than the area of the counter electrode *CE* (known also as an auxiliary electrode) [1].

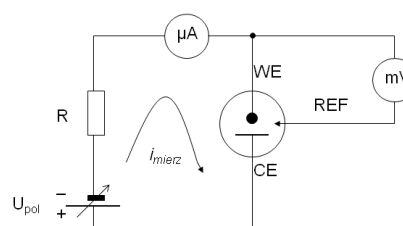


Fig. 1. The three electrode measurement system used in voltammetry
Rys. 1. Trójelektrodowy układ wykorzystywany do pomiarów woltamperometrycznych

The measured current consists of four components: diffusion, migration, convection and capacity component. It is given by:

$$i_{measu}(t) = i_{dyf}(t) + i_{migr}(t) + i_{conv}(t) + i_C(t), \quad (1)$$

where the sum is equal to:

$$i_{measu}(t) = z_i F S D_i \frac{c_i}{\delta} + \frac{z_i F c_i E}{RT} + c_i dV_i + V_i dc_i + C \frac{dU}{dt} + U \frac{dC}{dt}, \quad (2)$$

where:

- c_i – concentration of analyte,
- t – time,
- N_i – volume flux,
- D_i – the diffusion coefficient,
- z_i – ion charge,
- F – the Faraday constant,
- μ – mobility of species,
- U – potential,
- S – area of working electrode,
- E – potential,
- R – the gas constant,
- V – volume,
- T – temperature.

The most important component, in aqua solutions measurements, is the diffusion component. It has the highest value from among all the components. Thus the value of the diffusion component determines the value of the measured current [1].

Voltammetry is used for aqua solutions. The problems begin when the measured medium is not the aqua solution, but for e.g. soil. This problem has received no attention yet. In voltammetry, the mechanism of ion transport in aqua solution is well known and described, but there are no data concerning measurement of heavy metal ions in soil.

This preliminary study does not present the mechanism of ion transport in soil. It is believed that the mechanism of ion transport in water is similar to that in soil. Thus for soil measurement, the most important aspect is water content in soil. The diffusion coefficient should be different for soil and water measurement. In this case, the increased sensitivity of the method is needed. It should increase the concentration of heavy metal ions near the working electrode. Concentration of heavy metal ions near the working electrode will be increased, when the working electrode is polarized by large and opposite sign voltage. The change in construction of the measurement system may cause an increase in the concentration near the working electrode, too. There should be some extra electrodes to increase potential gradient of the electric field near the working electrode to change the system. This can improve the migration of heavy metal ions to the working electrode [3].

The value of the measured current depends on, inter alia, the diffusion component, according to equation (2). The measured current will have the highest magnitude, when the diffusion current equals the limit current according with the following equation [1, 2]:

$$i_{gr} = i_{df} = z_i F S D_i \frac{\partial c}{\partial \delta} = z_i F S D_i \frac{c^0}{\delta}, \quad (3)$$

The diffusion current will equal the limit current, if the concentration of heavy metal ions is equal to zero near the working electrode. Considering the diffusion layer thickness, the diffusion coefficient can be presented as:

$$D_i = \frac{i_{gr}^2 N_i}{z_i^2 F^2 S^2 c^0}, \quad (4)$$

Based on the above relation, if the measurement is made under constant conditions, the diffusion coefficient value can be expressed by a function only of the limit diffusion current. The constant conditions mean the same measurement system (with the same electrodes and the same distance between them), temperature and quality of water and reagents.

3. Materials and methods

Voltammetry and chronoamperometry were used to determine heavy metal ions in soil.

Before the laboratory verification, the soil had been washed. First, the soil was mixed and shaken out with the distilled water, and, next, decanted. This procedure was repeated three times. After that, the soil was dried to sand structure.

All voltammetric experiments were made by using an AUTOLAB with GPES and FRA software in 60 mm length square box made of plexiglas. The working electrode had 3 mm diameter, the auxiliary electrode had 25 mm diameter, both were made of carbon. One electrode was the reference and auxiliary electrode.

In voltammetry an important issue is the rate of water contents. 222 g of dry soil was mixed, in sequence, with 1 ml, 10 ml, 20 ml and 40 ml of water. Voltammetry measurements were taken for all parts of water.

Next, soil with 1 ml, 10 ml, 20 ml and 40 ml of water was mixed with 1 ml of 0.01 M aqua solutions of heavy metal ions and measured. The measurements were made for zinc (II) nitrate (V), copper (II) nitrate (V), lead (II) nitrate (V) water solutions.

The heavy metal ions were measured by using the method A, B, C (voltammetry) and chronoamperometry. The method A was voltammetry without any modification in the range 0 to -4 V. The method B was voltammetry with $U=1.5$ V for 120 s before measurement and the method C was $U=1.5$ V for 240 s before measurement, with the same range.

4. Results and discussion

The most important results of voltammetry measurements are shown in Figs. 2 and 3. They were made for 40 ml of water.

40 ml of water is the minimal standard of humidity for 222 g of dry soil for voltammetry measurements. This water volume was set experimentally. There is the most distinct inflection point on the curves for 40 ml of water.

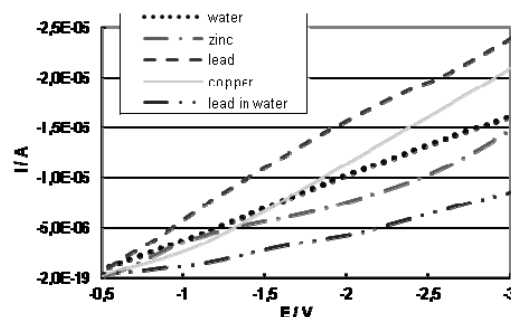


Fig. 2. The voltammetry result: method A for zinc, lead and copper ions in dry soil compared with soil with water (without ions) measurement
Rys. 2. Charakterystyka prądowo-napięciowa dla wyników metody A dla jonów miedzi, cynku i ołowiu w nawilżonej glebie porównane dla pomiarów gleby z wodą bez dodatku jonów metali ciężkich

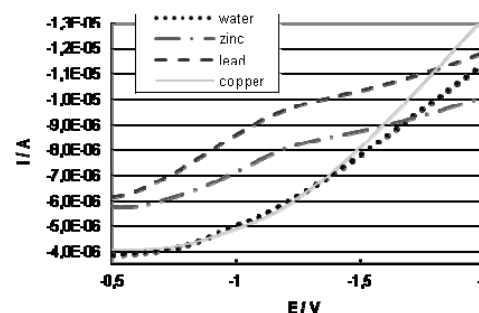


Fig. 3. The voltammetry results: method C for zinc, lead and copper ions in dry soil compared with soil with water (without ions) measurement
Rys. 3. Charakterystyka prądowo-napięciowa dla wyników metody C dla jonów miedzi, cynku i ołowiu w nawilżonej glebie porównane dla pomiarów gleby z wodą bez dodatku jonów metali ciężkich

Figs. 2 and 3 illustrate the results of voltammetry measurements with and without modification. Fig. 2 presents the curves for zinc, lead and copper ions, which were measured in soil. These curves show that there is no distinction between the zinc curve, copper curve and lead curve.

The method A (Fig. 2) is not good enough to make distinction between heavy metal ions in soil. The method B gives better results, but not good enough to see the difference between inflection for heavy metal ions measured in soil.

The method B and C were used for the same heavy metal ions. There are two different inflection points for the zinc and lead curve obtained by the method C (Fig. 3).

The method C is better for making distinction between heavy metal ions in soil. Voltammetry is useful for heavy metal ion measurements, but there is a need to polarize the working electrode before measurements.

Figs. 4 and 5 illustrate the results of the chronoamperometry. The graph in Fig. 4 shows the difference between the chronoamperometry heavy metal ion measurements in soil and water. Fig. 5 shows the difference between the chronoamperometry zinc and lead ion measurements in soil.

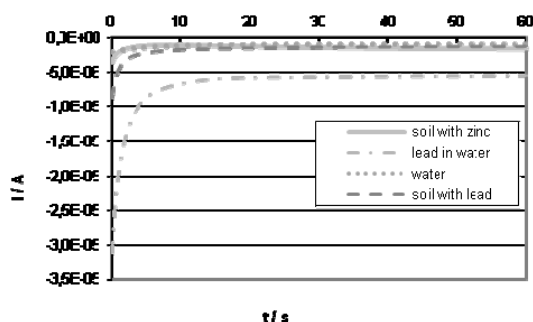


Fig. 4. Chronoamperometry results for zinc and lead in soil, lead in water and dry soil

Rys. 4. Chronoamperogramy dla pomiarów cynku i ołowiu w glebie, ołowiu w wodzie oraz dla nawilżonej gleby

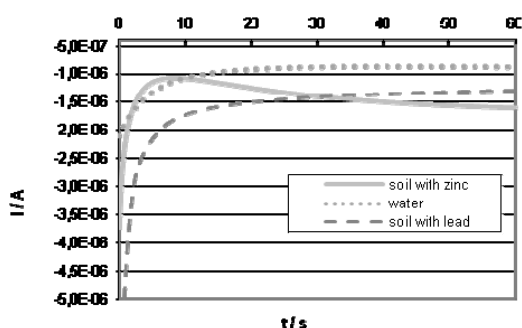


Fig. 5. Chronoamperometry results for zinc and lead in soil, and also for dry soil

Rys. 5. Chronoamperogramy dla pomiarów cynku i ołowiu w glebie, oraz dla nawilżonej gleby

The diffusion coefficient was calculated from the chronoamperometry measurements, for lead (II) nitrate (V) measured in water is $1.596 \cdot 10^{-4} \text{ m}^2/\text{s}$, and measured in soil is $8.487 \cdot 10^{-6} \text{ m}^2/\text{s}$ (for moisture soil).

5. Conclusion

The presented work improves the electrochemistry methods like voltammetry or chronoamperometry. It is useful for detection of heavy metal ions in soil. However, there are some problems with selectivity and sensitiveness. It is necessary to modify the measurement system.

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