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DETERMINATION OF AVAILABLE FORMS OF THE MANGANESE IN SOILS BY STRIPPING VOLTAMMETRY

OZNACZANIE MANGANU PRZYSWAJALNEGO W GLEBACH METODĄ WOLTAMPEROMETRYCZNĄ

Abstract: Conditions of determination of manganese(II) in soils samples using differential pulse cathodic stripping voltammetry in an electrochemically enriched solution (DPCSV-EE) at hanging mercury drop electrode have been optimized. Manganese was extracted from soils with 1 mol$\cdot$dm^{-3} HCl. 0.2 mol$\cdot$dm^{-3} ammonia/ammonium chloride buffer (pH = 8$\div$9) was supporting electrolyte. Deposition time was 15$\div$30 s, deposition potential -1.7 V, initial potential -1.15 V and end potential -1.7 V vs. NEK. In the above conditions Mn(II) peak height vs. its concentration dependence is linear up to $7 \cdot 10^{-5}$ mol$\cdot$dm^{-3} Mn(II). The accuracy and precision of the proposed method are also satisfactory. The relative standard deviation for 90 ppm Mn(II) equals 12.8% and for 145 ppm equals 8.9%. The method has been applied to study the content of available forms of the manganese in soils from the vicinity of Zawiercie Steel Mill and Huta Glogow Smeltery.

Keywords: available manganese, stripping voltammetry, soils extracts

Manganese is a trace element, which plays a significant role in metabolizm of plants. Most importantly, it is involved in oxidation-reduction reactions [1]. Thus, the level of manganese in soils in agricultural areas needs to be monitored. Currently, in Poland available forms of manganese are determined with the use of spectrophotometric and spectrometric methods [2, 3].

Stripping voltammetry is one of more sensitive methods used in trace analysis. It has an advantage over typical methods like spectrometric ones because the cost of electroanalytical equipment is rather low. Many voltammetric procedures have been proposed for the determination of trace amounts of manganese: by adsorptive stripping voltammetry [4, 5], by differential pulse anodic stripping voltammetry [6, 7], by differential pulse voltammetry [8-10], by square wave voltammetry [11-14] and by differential pulse cathodic stripping voltammetry in an electrochemically enriched solution (DPCSV-EE) [15-17]. In the present paper possible application of DPCSV-EE method for determination of available forms of manganese in soil extracts was analyzed. Manganese were extracted from soil using 1 mol$\cdot$dm^{-3} HCl. The method has been applied to study the degree of contamination of soils in the vicinity of Zawiercie Steel Mill and Huta Glogow Smeltery as well as Kornik reference area with manganese.

Experimental

Reagents

Hydrochloric acid, ammonia ("Suprapur", Merck), ammonium chloride (POCh, Poland). Ammonia + ammonium chloride buffer solution (pH 8$\div$9) prepared by mixing

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appropriate amounts of 0.4 mol·dm^{-3} NH$_3$ and 0.4 mol·dm^{-3} NH$_4$Cl. Standard solution of Mn(II) (1 g·dm^{-3}) were prepared from ampoules (Merck). Solutions with concentrations below 10^{-3} mol·dm^{-3} were prepared just before use. Water was doubly distilled in a quartz still.

Apparatus

Voltammetric measurements were carried out using a µAUTOLAB analyzer (ECO CHEMIE, Netherlands). A hanging mercury drop electrode (HMDE), having the surface of 3 mm^2, produced by Laboratorni Pristroje (Czech Republic), was the working electrode, KCl saturated calomel electrode (SCE), produced by Radiometer (Denmark), was the reference electrode, and Pt wire served as the counter electrode.

Procedures

Soil samples were taken from the top layer of soil: at the depth of 0÷20 cm for the copper mining area and Kornik and at the depth of 20÷40 cm for the Zawiercie. The soil was dried then homogenized and sieved through a mesh of 1 mm pore size. 10 g of soil was put into a 250 cm^3 bottle. 100 cm^3 of 1 mol·dm^{-3} HCl was added and the soil was shaken for 1 hr on a mechanical shaker. The extract was then filtrated.

1 to 3 cm^3 of the extract was put in a 25 cm^3 standard flask. The residue was diluted in 0.2 mol·dm^{-3} ammonia/ammonium chloride buffer solution. The pH was adjusted to 8÷9.

20 cm^3 of solution was transferred into a measuring vessel. After deaeration of the solution with purified nitrogen the manganese was deposited on the surface of electrode for 15 to 30 s (depending on the expected manganese content) at –1.70 V in stirred solution. 5 s after the stirrer, the potential was switched to the value –1.15 V and the reformed manganese(II) ions were determined by differential pulse cathodic voltammetry, within the potential range from –1.15 to –1.70. This cycle was repeated thrice. Mn(II) concentrations were determined using triple standard addition.

Results and discussion

Method of Mn(II) determination in ammonia/ammonium chloride buffer solution by differential pulse cathodic stripping voltammetry in an electrochemically enriched solution (DPCSV-EE) was prepared in the previous study [17]. It was used to assess the total manganese content in soils, ie manganese content in soil extracts obtained by using aqua regia extraction. The aim of the present study was to assess if previously prepared method allows to determine manganese available, ie manganese soluble in 1 mol·dm^{-3} HCl. Thus, influence of soil extract addition on analytic signal in determination of Mn(II) was checked.

This influence was analyzed by making a determination 2 ·10^{-5} mol·dm^{-3} Mn(II) in the presence of different amounts of soil extract. Experiments showed that maximum volume of the soil extract should not exceed 3 cm^3 (Fig. 1). With larger volumes of soil extract strong dampening of the manganese signal can be seen.

Using literature and present examination results optimal conditions for Mn(II) determination have been found.
- The base electrolyte: 0.2 mol·dm^{-3} ammonia/ammonium chloride buffer (pH = 8÷9)
- Deposition potential –1.7 V

- Initial potential –1.15 V
- End potential –1.7 V
- Deposition time 15÷30 s
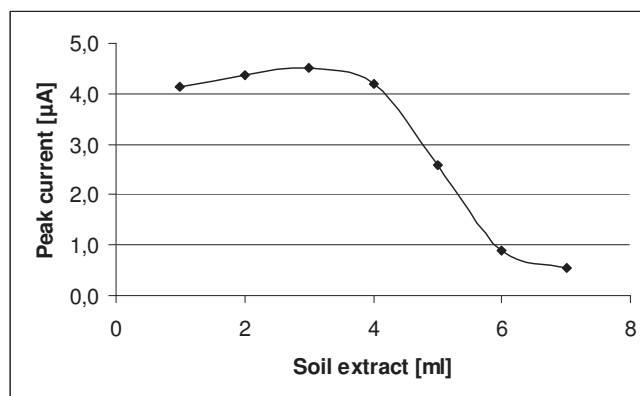- Amount of the soil extract added: 1 to 3 cm^3

Fig. 1. Dependence of the peak current for the Mn(II) on the amount of soil extract added. Mn(II) concentration $2 \cdot 10^{-5}$ mol·dm^{-3}. Supporting electrolyte 0.2 mol·dm^{-3} ammonia/ammonium chloride buffer (pH = 8÷9). Deposition potential –1.7 V. Initial potential –1.15 V. End potential –1.7 V. Deposition time 15 s

In the above conditions Mn(II) peak height vs its concentration dependence in the presence of 2 cm^3 of soil extract is linear up to $7 \cdot 10^{-5}$ mol·dm^{-3} Mn(II).

The developed method was statistically evaluated by estimating the precision and recovery manganese determined in the presence of soil extracts (Tab. 1). The recovery of added metal was very good and the precision was satisfactory (the relative standard deviation for 90 ppm Mn(II) equals 12.8% and for 145 ppm Mn(II) equals 8.9%).

Table 1

Recovery and precision of the determination of available forms of manganese in the analytical procedure

Series	Added [ppm]	Found [ppm]	Recovery [%]	S.D. [ppm]	R.S.D. [%]
I	90	88.3	98.1	11.3	12.8
II	145	136	93.8	12.1	8.9

Table 2

Manganese content in soil samples

Sampling regions	Depth [cm]	Research area	Mn available [ppm]	Mn total [ppm]
Copper mining area	0÷20	300 m south of Glogow Copper Smelter	82	106
	0÷20	600 m north of Glogow Copper Smelter	109	102
	0÷20	800 m north of Glogow Copper Smelter	85	166
	0÷20	3000 m north of Glogow Copper Smelter	36	33
Krakowsko-Czestochowska Upland	20÷40	2000 m north of Zawiercie Steel Mill	35	38
Kornik (reference area)	0÷20	Experimental Forest Zwierzyniec	82	134

The method has been applied to study the degree of contamination of soils in the vicinity of Zawiercie Steel Mill and Huta Glogow Smeltery with manganese (Tab. 2). For comparison results of determination of total manganese were presented in the last column [17].

Results show that manganese present in the examined soils poses no threat to plants and animals. According to Polish Branch Standard [3] available manganese content in soils equaled 9 to 110 ppm corresponds to soils of the III class of manganese content; such content is assessed as low.

Acknowledgment

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OZNACZANIE MANGANU PRZYSWAJALNEGO W GLEBACH METODĄ WOLTAMPEROMETRYCZNĄ

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Abstrakt: Przeanalizowano warunki oznaczania manganu(II) w próbkach gleb metodą woltamperometrii katodowej z elektrochemicznym wzbogacaniem (DPCSV-EE), w technice różnicowej pulsowej z użyciem wiszącej rtęciowej elektrody kroplowej. Mangan z gleb ekstrahowano roztworem 1 mol·dm^{-3} HCl. Elektrolitem podstawowym był 0,2 mol·dm^{-3} bufor amoniakalny (pH = 8÷9). Czas zatężania wynosił 15÷30 s, potencjał zatężania −1,7 V, potencjał startu −1,15 V, potencjał końcowy −1,7 V wzgl. NEK. W tych warunkach krzywa kalibracji jest prostoliniowa do 7 · 10^{-5} mol·dm^{-3} Mn(II). Dokładność i precyzja opracowanej metodyki są zadowalające (względne odchylenie standardowe dla 90 ppm Mn(II) wynosi 12,8%, a dla 145 ppm Mn(II) 8,9%). Opracowaną metodykę wykorzystano do analizy zawartości przyswajalnych form manganu w glebach, pochodzących z okolic Huty Miedzi Głogów i Huty Stali Zawiercie.

Słowa kluczowe: przyswajalny mangan, woltamperometria stripingowa, próbki gleb