

Letter to Editors

Spectrophotometric Determination of Iron (II) in the Soil of Selected Allotment Gardens in Łódź

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Abstract

The present work is a continuation of our research on the content of heavy metals in the soil of allotment gardens located in the area of Łódź. It presents results of the determination of bioavailable and total iron in the soil collected in two allotment gardens in the city. Iron was determined spectrophotometrically in the form of red-pink complex of Fe(II) and 2,2'-dipyridine.

The method of determination recommended by the Polish Standards has been modified by using hydroxylamine instead of glycine to reduce Fe(III) to Fe(II).

Keywords: iron (II), 2,2'-dipyridine, soil.

Introduction

Excessive, unnatural amounts of various chemical substances in addition to other heavy metals, disturb the operation of the complex system of processes in the soil and have an adverse influence on the circulation of elements in nature by decreasing or increasing the absorption of metals by plants. They may also lead to soil degradation, which has a negative impact on plants and consequently on food products and human health. Due to high concentration of iron in the earth crust, it is not classified as a trace element, although its levels in living organisms are low. Since it plays an important role in physiology, it belongs to the group of the so called bioelements - metals which are necessary for normal development of the living organisms. Iron plays a significant role in biological processes; it takes part in the synthesis of haemoglobin, myoglobin and iron-porphyrin enzymes. Its deficiency causes anaemia, and next atrophy of mucous membranes as a result of disturbed ab-

sorption of nutrients. The excess of iron in the living organisms practically does not lead to chronic poisoning, as it is accumulated in tissues in the form of inactive compounds with proteins [1-3].

The content of iron in the soil varies from a fraction of per cent to several per cent, and its concentration and distribution depend largely on the type of soil. Given the same general content of iron, in anaerobic conditions of acid soil an excess of its ions may have a toxic effect on plants, while in oxidative conditions of alkaline soil, a deficiency of the element may occur, caused by limited solubility of its compounds rather than by its insufficient level [4-6]. According to literature data [7-9], there are major differences in the concentration of iron in the soil in Poland; the content of total iron varies from 2,000 to 48,000 mg per kg of dry mass.

So far, there have been no investigations on the content of iron in the soil of the city of Łódź. The present work is a part of a research project to examine the content of heavy metals in the soil of the allotment gardens in Łódź [10-13].

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Experimental

Reagents

- concentrated chloric(VII) acid (Riedel-de-Haλn AG)
- 1.0 and 0.1 M hydrochloric acid
- stock standard solution of iron, concentration 0.100 mg/ml was prepared in the following way: 0.7022 g of ammonium iron(II) sulphate(VI) hexahydrate ($[\text{Fe}(\text{NH}_4)_2](\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in water in a 1000 ml flask, 10 ml of concentrated sulphuric(VI) acid was added and water was added to the mark.
- working standard solution of iron(II), prepared by diluting 25 ml of stock standard solution with a solution of 1 mole hydrochloric acid in a 500 ml flask. 1 ml of the solution contained 0.005 mg of iron(II).
- 10% solution of acetic acid (v/v)
- sulphuric(VI) acid, concentration 0.4 M
- 2,2'-dipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$) solution was prepared by dissolving 0.200 g of the compound in 100 ml of 10% solution of acetic acid.
- glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) (Fluka AG) solution was prepared by dissolving 0.100 g of glycine in 100 ml of 0.4 M sulphuric(VI) acid
- hydroxylamine (NH_2OH) solution was prepared by dissolving 0.100 g of hydroxylamine hydrochloride in 100 ml of 0.4 M sulphuric(VI) acid
- ammonia water prepared by diluting 25% (m/m) ammonia (P. Ch. Odczynniki - Lublin) with water, at 1:2 ratio (v/v),
- ammonium acetate, concentration 1 M.

Apparatus

High pressure one-stand microwave mineraliser Uni Clever BM-1z, spectrophotometer SPECOL 11 with cells 5 cm optical pathlength,

NB.: All reagents, apart from chloric(VII) acid, ammonia and glycine, were produced by POCh - Gliwice, and were prepared with the use of redistilled water.

Soil Sampling and Mineralisation

The original samples of soil were collected according to the standard procedure [14] from two allotment gardens in Łódź: "Krokus" (in the area of Drewnowska and Odolanowska streets) and "Władysław Reymont" (in the area of Sporna and Źródłowa streets). Laboratory soil samples were prepared according to the same standard procedure. Prior to mineralisation and extraction, the samples were left for two weeks in a dry and airy place and thus brought to a state of "air dryness".

Mineralisation of the samples of about 1.000 g each was carried out in a microwave mineraliser in a medium of concentrated chloric(VII) acid [15]. Total iron content was determined in the prepared solutions

In order to obtain solutions used for the determination of bioavailable iron, soil extracts were prepared. Samples of about 10.000 g of air dried soil were placed in poly-

ethylene dishes and the next 100 ml of 1 M hydrochloric acid was added, then the mixture was stirred for one hour in a magnetic bar stirrer [16].

Iron was determined spectrophotometrically in the obtained soil solutions in the form of a complex with 2,2'-dipyridine.

Principle of Determination

In a slightly acid medium, iron(II) ions form an electropositive red-pink complex with 2,2'-dipyridine [17,18]. Its molar absorption coefficient ϵ is $8.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$, at wavelength $\lambda = 522 \text{ nm}$. The solution of the complex is stable and Fe(II) bound in the complex with 2,2'-dipyridyl is resistant to oxidation. As only Fe(II) participates in the complex formation reaction, it is necessary to reduce the Fe(III) ions present in the reaction medium. Different agents may be used for this purpose: hydroxylamine, ascorbic acid, sulphate(IV), or glycine [18]. The reaction is carried out in the presence of sodium acetate or citrate, which prevents precipitation of easily hydrolysed cations. The reaction of Fe(II) and 2,2'-dipyridine has been used for determination of iron in alloys, minerals and food products [19-21].

Determination

In order to plot the calibration curve, portions of 0.00 to 10.00 ml of working standard solution of iron(II) were placed in 25 ml flasks, which corresponded with the amount of Fe(II) from 0.00 to 50.00 μg in the sample, respectively. Next, 1.5 ml of the mixture of the reducing agent and 2,2'-dipyridine solution was added and the solution was left for 10 minutes. Then, the reaction solution was completed with redistilled water to 10 ml and neutralised with ammonia water until stable colour was obtained. The solution was completed with ammonium acetate solution to reach a volume of 25 ml. The absorbance was measured after 30 minutes in 5 cm optical pathlength cells at wavelength $\lambda = 523 \text{ nm}$ against blank test as reference. A linear correlation between the concentration of the metal and absorbance is observed in the examined range of Fe(II) concentration (Fig. 1), with the correlation coefficient equal to 0.9986.

The procedure of determination of iron in the soil samples was analogous to that used for plotting the calibration curve, but instead of the working standard solution of iron(II), samples of 1.0 to 5.0 ml of mineralised or extracted soil were placed in the flasks. The content of iron "X" in the soil was calculated according to the following formula:

$$X = C_x \frac{V_1 \cdot 10000}{V_2 \cdot m} \text{ [mgFe/kg d.m.]}$$

Where: C_x – concentration of iron read from the calibration curve [mg/25 ml]

V_1 – total solution volume after mineralisation or extraction [ml]

V_2 – volume of the soil solution taken for analysis [ml]
 m – weighed amount of soil [g]

Results and Discussion

The spectrophotometric method of determination of iron in the form of a Fe(II) complex with 2,2'-dipyridine, recommended by the Polish Standards [16], was used to measure the content of the metal in the soil. Glycin (recommended by the standard procedure) was used to reduce Fe(III) ions. The results of the determination of total and bioavailable iron in the soil samples were considerably lower than those obtained for comparison by the method of atomic absorption spectrometry (a method which is also recommended by Polish Standards) (Table 1). Mean content of iron in Polish soils mentioned in literature [7 - 9] are similar to our results obtained by the comparative method. The increase of the reducing agent or the complexing agent did not significantly affect the results of the determination, which may suggest that Fe(III) was not entirely reduced to Fe(II). Therefore, we decided to change the reducing agent and use hydroxylamine hydrochloride instead of glycin. The rest of the analytical procedure remained the same as recommended in the Standards. The results are listed in Table 2. They demonstrate that hydroxylamine hydrochloride reduces more effectively Fe(III) ions present in the reaction medium to Fe(II). On average, the content of iron determined by the spectrophotometric method is by 10-15% lower than the content determined by the comparative method of atomic absorption spectrometry.

Compared with other metals, the amounts of iron in the soil are high (mean content of Fe - about 15,000 mg/kg dry mass, of lead - up to 100 mg, cadmium - up to 3.0 mg, zinc - up to 300 mg, copper - up to 100 mg/kg dry mass [22]). Therefore, their influence on the determination of iron by the spectrophotometric method is insignificant. It only seemed advisable to test the influence of the content of manganese, whose concentration in the soil is relatively high and may vary from 100 to 2000 mg/kg dry mass [4]. The results are presented in Table 3. They indicate that the amounts of manganese which may occur in the soil do not affect the results of determination of iron in the form of the

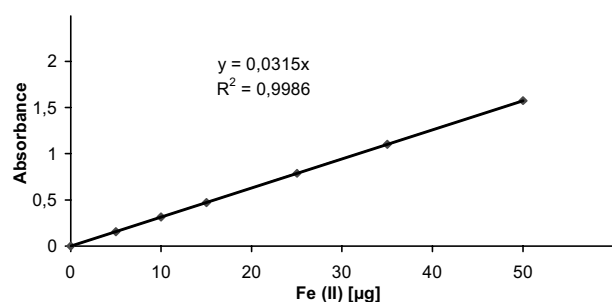


Fig. 1. The calibration line for determination of Fe(II) in the form of a complex with 2,2'-dipyridine.

Table 1. The content of bioavailable and total iron in the samples of soil, determined in the form of a complex with 2,2'-dipyridine with the use of glycin (1) and by the atomic absorption method (2) .

Soil sample	Bioavailable iron		Total iron	
	mg Fe/kg dry mass		mg Fe/kg dry mass	
	1	2	1	2
1	219	1750	485	16 600
2	171	1130	352	12 300
3	177	1820	163	11 300
4	191	1460	219	6 900
5	284	2210	339	16 600
6	247	1750	133	13 500
7	238	1925	159	10 800

Table 2. Comparison between the content of bioavailable iron(II) determined in the form of a complex with 2,2'-dipyridine with the use of different reducing agents (1) and the content of iron(II) determined by the atomic absorption method (2).

Soil sample	Iron content mg/kg dry mass		
	1		2
	Glycin	Hydroksylamine	
1	171	1 000	1 140
2	202	870	970
3	216	4 290	5 090
4	194	1 400	1 660
5	182	1 050	1 250
6	278	1 590	1 820
7	219	1 580	1 750

Table 3. The influence of Mn(II) content on the amount of Fe(II) determined in the form of a complex with 2,2'-dipyridine.

Mn (II) amount introduced into the sample [µg]	Fe (III) introduced into the sample [µg]	Fe(II) determined in the sample [µg]	Error [%]
0.00	25.00	24.89	0.44
5.00	25.00	24.63	1.48
10.00	25.00	24.75	1.00
15.00	25.00	24.68	1.28
20.00	25.00	24.85	0.60
25.00	25.00	24.87	0.52

complex with 2,2'-dipyridine.

Our work presents the results of spectrophotometric determination of the content of bioavailable and total iron in the samples of soil collected in two allotment gardens in Łódź. Tables 4 and 5 list the content of iron in the soil from the "Krokus" and "Władysław Reymont" allotment gardens, respectively. Total content of iron varied, depending on the place of sample collection and the garden, from 6700 to 15000 mg/kg dry mass, which, according to literature data,

Table 4. Content of bioavailable and total iron in the soil samples collected in the "Krokus" allotment garden.

Soil sample	Mean iron content [mg/kg dry mass]	
	total	bioavailable
1	15 050	2 060
2	12 950	1 690
3	7 200	1 300
4	10 500	1 940
5	11 700	1 570
6	9 650	1 585
7	13 220	1 730

Table 5. Content of bioavailable and total iron in the soil samples collected in the "Władysław Reymont" allotment garden.

Soil sample	Mean iron content [mg/kg dry mass]	
	total	bioavailable
1	9 800	1 455
2	8 420	1 465
3	9 970	1 925
4	9 780	1 600
5	6 710	1 025
6	8 620	1 380
7	7 960	1 290

Table 6. A list of results of determination of iron in the "Władysław Reymont" allotment garden.

Soil sample	Mineralised samples	Samples extracted with 1 mole HCl	Samples extracted with 0.1 mole HCl	Samples extracted with H ₂ O	Iron content [mg/kg dry mass]
1	9 800	1 455	84.2	14.0	
2	8 415	1 465	89.9	15.5	
3	9 970	1 925	79.9	17.5	
4	9 780	1 600	71.5	13.7	
5	6 705	1 025	88.1	9.8	

means that the soils present a natural and most common levels of iron content. The amounts of bioavailable iron depended on the place of sample collection and varied from 1000 to 2000 mg/kg dry mass.

No relation was observed between the acidity of the soil and the content of iron (pH about 6.7 to 7.3). According to the classification of the Polish Standards, this means that the soil in the gardens belong to the second class of iron content and contain mean amounts of the metal. The ratio between bioavailable and total iron was from 5:1 to 8:1, which implies that only a small portion (up to 20%) of the metal present in the soil may be absorbed by the plants. A major part of iron present in the soil occurs in the forms which are not available to plants. This is confirmed by the data presented in Table 6. Additionally, it contains the results of determination of iron after extraction with 0.1 M solution of hydrochloric acid and redistilled water. According to Polish Standards, bioavailable forms of iron are those which are soluble in the medium of 0.1 M hydrochloric acid solution. Since the soil solutions are far less sour, solubility of this metal was examined also in the medium of 0.1 HCl (according to some authors some soils are very acid, with pH \approx 3 [23, 24], and locally, in the root zone even lower) and redistilled water (a medium which is most similar to natural soil solutions). In the samples extracted with 0.1 M hydrochloric acid, the content of iron was within the range of 65 to 90 mg/kg dry mass, which was 1.3% of total iron in the soil at the utmost. In the samples extracted with water the content of iron was from 9.8 to 17.5 mg/kg dry mass, which was 0.18% of the total content of the metal. These data confirm that only a very small portion of iron present in the soil occurs in bioavailable forms.

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