Development of a Method for Measuring the Content of Extractables Mn(II) Forms in Soils Using Periodate Ions for Environmental Monitoring Purposes

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Abstract. The article presents the results of the development and preparation for metrological certification of methods for measuring the content of extractable forms of manganese (II) in soils, establishing its minimum detectable concentrations. It is established that the use of potassium periodate has a number of significant advantages: the determination procedure is less toxic compared to the use of formaldoxime, solutions have a more stable color over time, it is not necessary to eliminate the interfering influence of chloride ions. The experiment is carried out to establish the metrological characteristics (indicators of precision, accuracy, and precision) with the use of work samples of different soil types. The metrological characteristics of the results are not worse than those regulated by the regulatory document for the certified method.

1. Introduction
Heavy metals play a special role in the biosphere, are one of the main factors of modern production and its anthropogenic impact on the environment. Therefore, it is necessary to constantly monitor the content of heavy metals in the soil. In addition, it is known that excessive soil acidity, as well as a low content of exchange forms of calcium and magnesium, a high concentration of mobile compounds of aluminum, iron and manganese adversely affects the colloidal and buffer properties of the soil-absorbing complex [1].

2. Relevance, scientific significance
Soil analysis methods are sufficiently developed to determine the content of a wide range of elements. At the same time, the development of new algorithms and methods for soil analysis that meet modern metrological requirements is an urgent task of practical significance.

Agrochemical services to determine the content of manganese (II) ions in the soil use certified methods (hereinafter MM), for example, the total content is determined by non-destructive methods of research (X-ray fluorescence and atomic absorption spectroscopy).

Determination of other forms of manganese is carried out using measurement methods based on the photometric method of analysis. As a reagent, the use of formaldoxime is provided. During the implementation of the algorithm, the analytical signal caused by the formation of a complex connection is evaluated.

In the literature [2] there are two points of view on the composition of the resulting complex:
1. Formaldoxime in an alkaline medium interacts with manganese (II) cations, first a colorless complex is formed, then the oxidation by O₂ from air leads to a red-brown complex Mn(IV) – [Mn(CH₃NO₂)₆]²⁺ with an intense absorption band λmax = 455 nm, εmax = 1,12·10⁴.

2. During the determination, the metal ion is oxidized to the trivalent state Mn(III), and the composition of the resulting complex corresponds to the formula Mn(CH₃NO₂)₃.

The color is formed within a few minutes and is stable for more than 16 hours. The maximum light absorption of the formaldoximate complex of manganese, which changes with increasing temperature and pH of the medium, can be stabilized by adding tartaric acid at pH 10-13. The method is used to determine the content of manganese (II) in soil extracts, plant materials, alloys, cements, and water.

In the presented methods, formaldoxime is used in the presence of ammonia solutions with high concentrations, which leads to an increase in the toxicity of the determination procedure. Other reagents can also be used for Mn²⁺ oxidation, such as KIO₄, PbO₂, NaBiO₃ and (NH₄)₂S₂O₈.

Most certified spectrophotometric methods for determining the content of manganese(II) are based on the oxidation of manganese ions Mn²⁺ to MnO₄⁻ in a nitric acid medium using ammonium persulfate in the presence of an AgNO₃ catalyst, followed by measuring the optical density of the solution at λ = 540 nm and using a calibration curve:

\[ 2\text{Mn}^{2+} + 5\text{S}_2\text{O}_8^{2-} + 8\text{H}_2\text{O} = 2\text{MnO}_4^- + 10\text{SO}_4^{2-} + 16\text{H}^+ \]

Determination of the content of manganese (II) using ammonium persulfate is hindered by the presence of chloride ions, which are oxidized by the reaction equation:

\[ 2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

Also, when using certified methods with ammonium persulfate, the determination of manganese(II) content is hindered by the presence of organic substances:

\[ \text{RCOOH} + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 \uparrow + \text{H}_2\text{O} \]

It is known that manganese (II) can form complex compounds with organic substances (amines, organic acids, amino acids, humus substances) contained in water. They are usually less strong than similar compounds with other transition metals, but the resulting coordination compounds may reduce the reliability of the results obtained [3].

When analyzing soils, different extraction solutions are used to determine different forms of manganese in the methods: mobile manganese is extracted by CH₃COONH₄, exchange – KCl, so the use of persulfate as a universal reagent is difficult to implement.

It is often suggested to use KIO₄ as an oxidizer, while the determination of manganese (II) content is not affected by the presence of chloride ions and organic substances [4, 5], and solutions have a more stable color than when oxidized with ammonium persulfate.

The oxidation of the determined ion proceeds according to the following equation:

\[ \text{Mn}^{2+} + \text{IO}_4^- + 3\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + \text{IO}_3^- + 6\text{H}^+ \]

Determination of manganese (II) ions using potassium periodate as an oxidizer has a number of significant advantages:
- ability to detect manganese in various objects
- the determination procedure is less toxic than using formaldoxime
- there is no need to eliminate the interfering influence of chloride ions and organic substances, which greatly simplifies the analysis
- solutions have a more stable color over time than when oxidized with ammonium persulfate
- the method is quite simple to perform and does not require time.

Therefore, the purpose of the study was to develop and prepare for certification of methods for determining the content of exchangeable and mobile manganese in soils, substantiate the measurement conditions and establish the boundaries of the determined concentrations.
3. Research result

Based on the literature data and the analysis of certified methods, algorithms for determining exchangeable and mobile manganese in soils in the presence of potassium periodate are proposed (Table 1).

| Exchange manganese | Mobile manganese |
|---------------------|------------------|
| 30.0 g of soil, 75 cm³ KCl (stir on the rotator for 1 hour) the aliquot volume - 5 cm³ | 5.0 g of soil, 50 cm³ CH₃COONH₄ (stir on the rotator for 1 hour) the aliquot volume - 5 cm³ |
| + 7 cm³ Na₄P₂O₇·10 H₂O +5 cm³ CH₃COONH₄ +2 cm³ KIO₄ | |

The induction period is 7 minutes
The induction period is 20 minutes

Measurement conditions: \( \lambda = 530 \text{ nm}, l = 20 \text{ mm} \)

The ranges of definitions for certified methods are in the range from 10 to 132 million\(^{-1}\). The molar absorption coefficient of permanganate ions is 5 times less than that of the Mn(II) complex with formaldoxime, i.e. the determination of the mass concentration of Mn(II) in the case of obtaining an analytical signal due to MnO₄\(^{-2}\) ions is less sensitive. Therefore, to establish the measurement range, the possibility of determining manganese ions in various forms at low concentrations (≤ 10 million\(^{-1}\)) was studied by photometric method in the presence of KIO₄. Table 2 shows the concentration of calibration solutions.

| No | Mobile Mn | Exchange Mn |
|----|-----------|-------------|
|    | Aliquot part of the working solution (cm³) with C = 100 mcg/cm³ | The concentration of ions of Mn, million\(^{-1}\) | Aliquot part of the working solution (cm³) with C = 110 mcg/cm³ | The concentration of ions of Mn, million\(^{-1}\) |
| 1  | 0,20      | 2           | 1,0          | 1,1          |
| 2  | 0,40      | 4           | 2,0          | 2,2          |
| 3  | 0,60      | 6           | 3,0          | 3,3          |
| 4  | 0,80      | 8           | 5,0          | 5,5          |
| 5  | –         | –           | 8,0          | 8,8          |

Calibration dependences \( A = f(C) \) in the specified range of concentrations of exchangeable and mobile manganese are obtained. For calculations experimental dependencies \( s_A = f(A) \) were used.
Measure of the determined minimum was considered to be the coordinates of the intersection point of the lines $s_\Lambda = f(\Lambda)$ and $\Lambda = 5 \cdot s_\Lambda$. The number of parallel determinations was five (Fig. 1).

**Figure 1.** Determined minimum of the method for measuring the content of manganese in soils using periodat-ions: 1) $s_\Lambda = f(\Lambda)$ – experimental (LSM); 2) direct $\Lambda = 5 \cdot s_\Lambda$

a) mobile ($l = 20$ mm); b) exchange ($l = 50$ mm).

From the data obtained, it follows that the developed method can determine concentrations below those specified in certified methods (mobile – from 5.8 million$^{-1}$ at $l = 20$ mm or from 2.3 million$^{-1}$ at $l = 50$ mm; exchange – from 2.3 million$^{-1}$ at $l = 50$ mm). It was found that the reagent used for the extraction of various forms of manganese does not affect the analytical signal due to the $\text{MnO}_4^-$ color.

Based on the proposed algorithms, a method for measuring the concentration (MM) of extractable forms of manganese(II) in soils has been developed. For the purpose of further certification of MM, an experiment was conducted to establish metrological characteristics (precision, correctness and accuracy indicators) in accordance with metrological recommendations. Working samples of various types of soil were selected for the experiment. After sampling and sample preparation according to [6], the analytical signal was measured and the results were processed.

A statistical experiment was performed using soil extracts according to the proposed algorithms [7-10]. To establish the repeatability index, the results of a single analysis within each series were obtained under the same conditions and almost simultaneously. When conducting an experiment in conditions of intra-laboratory precision, experimental data were obtained by varying all the factors that form intra-laboratory precision (a series of results of a single analysis was obtained at different times, using different batches of reagents of the same type, different sets of measuring utensils). To establish the accuracy and correctness indicators, the methods were selected using a control method (which was the corresponding certified method), and the method of additives. The calculated characteristics are shown in table 3.
Table 3. Measurement range, values of repeatability, intra-laboratory precision, accuracy and accuracy of measurements.

| Measurement range Mn, million\(^1\) | Repeatability indicator \((P=0.95), \sigma_r, \%\) | Indicator of intra-laboratory precision \((P=0.95), \sigma_{R_{I}}, \%\) | Accuracy index \((P=0.95), \pm\Delta_r, \%\) | Accuracy index \((P=0.95), \pm\Delta_{I}, \%\) |
|-------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| Mobile manganese                    |                                               |                                               |                                               |                                               |
| from 3 to 50 incl.                  | 0.9                                           | 1.2                                           | 8                                             | 20                                            |
| more than 50                        | 1.9                                           | 2.3                                           | 15                                            | 25                                            |
| Exchange manganese                  |                                               |                                               |                                               |                                               |
| from 3 to 132 incl.                 | 1.1                                           | 1.3                                           | 12                                            | 25                                            |

4. Conclusions

Thus, algorithms for determining manganese in soils in the presence of potassium periodate are proposed, methods for measuring the content of exchangeable and mobile manganese in soils are developed, metrological characteristics of the created methods are calculated (repeatability, intra-laboratory precision, correctness, accuracy). It was found that the use of potassium periodate as an oxidizer for the quantitative determination of manganese has a number of significant advantages compared to the determination of the content in the presence of formaldoxime (with equal accuracy characteristics of the results obtained).

5. References

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