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Research Article

# Spectrophotometric Determination of Exchangeable (Mobile) Aluminum in Soil Using Arsenazo I

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**Abstract:** The possibility of using arsenazo I as a reagent for the spectrophotometric determination of the content of exchangeable (mobile) aluminum in soils of various types (clay, loamy, sandy, and sandy loam) is considered. An algorithm of analysis has been developed, taking into account the methodological guidelines MGU 4.1.2466, calibration dependencies have been established, and soil samples have been analyzed according to certified and proposed experimental methods. As a certified methodology, the methodology for performing measurements of GOST 26485 “Soils. Determination of exchangeable [mobile] aluminum by the SICAA method”, in which one of the reagents is xylene orange has been used. To determine the effect of soil type on the results of aluminum determination, samples with different humus content and metabolic acidity were analyzed, and an artificial soil humification Al(III) reagent was used to study the effect of organic compounds on the analytical signal. It was determined that humus affects the measurement results only when its content is significant. It has been established that the use of arsenazo I for the spectrophotometric determination of exchangeable (mobile) aluminum in soil is possible along with the reagents provided by a certified measurement technique-xylene orange and chromazurol C. A number of advantages of using arsenazo I to determine the content of mobile aluminum have been established.

***Keywords*:** aluminum, soils, arsenazo I, spectrophotometry, humus

## 1. Introduction

The content of mobile aluminum is one of the indicators of soil quality, on which the intake of minerals into plants depends. Aluminum in the soil plays an important constitutional role, and participates in the formation of potential acidity. The increased content of aluminum in the soil has a negative effect on plants due to the formation of insoluble phosphates, which reduces the intake of potassium, calcium, magnesium, phosphorus, and iron into plants and reduces their water consumption.[1,2]

Free aluminum ions in toxic concentrations cause great harm to cultivated plants. This metal is considered to be the main toxic element in the cultivation of plants on acidic soils, which accounts for about 40% of the total area of arable land. Therefore, it is necessary to constantly monitor its content in the soil matrix.[3-5]

Since the $Al^{3+}$ ion does not have a chromophore effect, only colored reagents are used for its quantitative photometric measurements. To determine the content of the aluminum ions, triphenylmethane dyes are widely


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used, forming sufficiently strong complexes with the studied ion, the maximum light absorption of which lies in the wavelength range from 500 to 600 nm. The determination of the content of mobile aluminum is carried out according to the certified measurement method GOST 26485-85 “Soils. Determination of exchangeable [mobile] aluminum by the SICAA method”, which provides the reagents chromazurol C or xylene orange (XO) for the photometric determination, which relates to triphenylmethane dyes. Chromazurol C is a fairly sensitive one (molar light absorption coefficient 59,300), but it is a more expensive reagent. In the case of xylene orange, the detectable minimum decreases ($\varepsilon \sim 21{,}100$), and the equilibrium time of the reaction of complexation of the reagent with $Al^{3+}$ ions increases significantly (up to 2 hours), which makes this reagent not convenient to be used in flow analysis.[3] However, this technique is characterized by insufficient accuracy: the total relative error of determination is 30% for the number of equivalents from (⅓ $Al^{3+}$) to 0.12 mmol per 100 g of soil.

According to Kolosova,[6] such indicators as ferron, eriochromocyanine R, methylthymol blue, pyrocatechin violet, and arsenazo are also proposed to determine the concentration of aluminum by the photometric method. The course of aluminum complexation reactions with these indicators requires less time, for example, the Al(III) complex with arsenaso I is formed within 15 minutes. The use of this indicator is based on the certified method to measure the aluminum content in the dust of explosives in the air of the working area of MGU 4.1.266-09. In this respect, the purpose of this work is to develop an algorithm for determining the content of mobile aluminum in soils using arsenazo I, to establish the boundaries of its applicability, and to assess the influence of the matrix of analyzed objects on the results of determination.

## 2. Materials and methods

The results of the study were obtained using spectrophotometric and X-ray fluorescence analysis methods.

During the study, an experiment was conducted according to the following Figure 1:

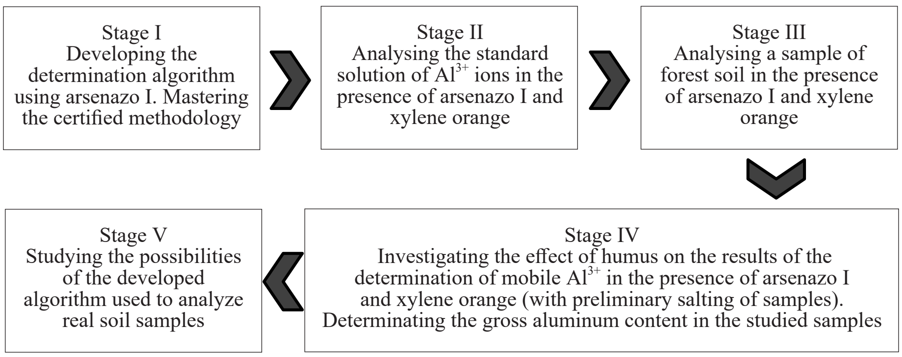


**Figure 1.** Experimental design

To plot calibration dependencies and test the proposed algorithm, standard solutions certified according to the preparation procedure from state standard samples or those prepared by dissolving the exact suspension of aluminum salt were used. Prepared standard solutions were also used to add additives. To add humus, the preparation ECO HUMUS from Leonardite with trace elements was applied. The value of the humus content in the obtained samples was determined by the spectrophotometric method.

The experiment was repeated on samples of real soils of various types. The working samples were selected in such a way that the range of acidity of their salt extract (from 4 to 6 pH units) and the humus content varied as much as possible (from 0 to 35%).

Quality control of the results was carried out using control samples and the method of additives.

When processing data and plotting dependencies, the Microsoft Excel software package was used.

## 3. Results

Taking into account MGU 4.1.266-09, an algorithm for the determination of aluminum with arsenazo I in soils has been developed: obtaining a salt extract of soil using 1 N potassium chloride solution; adding the necessary reagents to form an Al(III) complex with arsenazo I and eliminating the influence of interfering substances; carrying out photometry of solutions. Then the calibration graphs were built according to both GOST 26485-85 and the developed algorithm using a PORTLAB spectrophotometer model 501. The algorithm was tested using arsenazo I on a standard aluminum(III) solution.

Table 1 shows the results of determining the aluminum content in a standard solution. Each result is the arithmetic mean of two results of parallel determinations that have passed the procedure of operational repeatability control.

**Table 1.** Results of determination of aluminum content in standard solution, C (⅓ $Al^{3+}$) = 0.19 mmol/100 g of soil*

| Methodology | Results of parallel determinations C (⅓ $Al^{3+}$), mmol/100 g of soil | | $C_{av.}$ (⅓ $Al^{3+}$), mmol/100 g of soil | Precision control |
|---|---|---|---|---|
| Experimental | 0.18 | 0.17 | 0.18 | $K_K = 0.01 = K = 0.01$ |
| Certified | 0.20 | 0.18 | 0.19 | - |

*The error of determination is 5% (corresponds to GOST 26485)

Based on the analysis of the presented aluminum concentration values, it was found that the result obtained with arsenazo I differs slightly from the value obtained by the certified method. In addition, the aluminum content according to the experimental method is closer to the certified one according to the preparation procedure.

To determine the content of mobile aluminum(III) in the soil sample, the forest soil with the least amount of substances interfering with its determination was used. Table 2 shows the results of the determination. The values are obtained under repeatability conditions.

**Table 2.** The results of determining the content of mobile aluminum(III) in a sample of forest soil (mmol/100 g of soil)

| Methodology | Results of parallel determinations C (⅓ $Al^{3+}$) | | $C_{av.}$ (⅓ $Al^{3+}$) |
|---|---|---|---|
| Certified | 0.14 | 0.15 | 0.15 |
| Experimental | 0.17 | 0.18 | 0.18 |

The values of the results of the analysis of a real object, established using a certified methodology and an experimental technique with arsenazo I, differ by 20%, which can be explained by the influence of organic substances (humus) contained in the soil.[7-8]

The regulatory document provides the elimination of the interfering effect of organic substances by ashing. To clarify the nature of the effect of humus on the results obtained, artificial enrichment of forest soil with it was carried out. To determine the humus content in the working soil samples, a calibration dependency was used: A = 0.0473 C (carbon), mg, obtained at $\lambda$ = 590 nm, l = 10 mm (conversion coefficient to humus 1.728). It is shown that under these conditions, the content of aluminum(III) in the soil cannot be determined with any of the indicators. This is due to the intensive complexation of Al(III) with the introduced humic substances and the transition of the mobile form of aluminum(III) to the gross one. To confirm this conclusion, the mineralization of a full-scale soil sample was carried out, followed by the determination of the gross aluminum content using xylene orange according to the certified methodology and the experimental technique with arsenazo I. The reference value (gross content) was determined using

X-ray fluorescence analysis. Figure 2 shows the results of the determination.

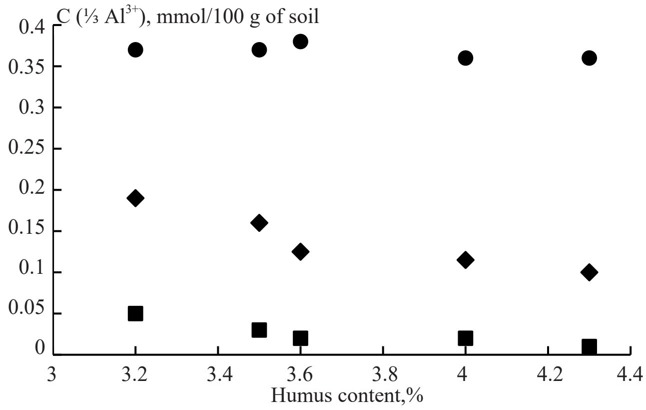


**Figure 2.** The results of determining the total aluminum content in artificially gummed soil by X-ray fluorescence analysis (●) and by the spectrophotometric method (◆-in the presence of arsenazo I; ■-using xylene orange) after mineralization

It can be seen from Figure 2 that the results of the determination of Al obtained using arsenazo I and xylene orange are different. It can be concluded that arsenazo I is more suitable for determining the gross aluminum content.

To study the effect of increased humus content at varying values of metabolic acids for different types of soils, the results of analysis of soil samples of various types in the presence of xylene orange (XO) and arsenazo I were obtained (Table 3). The measurement results of quality indicators represent the arithmetic mean of the definitions obtained under repeatability conditions.

**Table 3.** The results of determining the content of mobile aluminum in various types of soils

| Soil type | pH | Humus,% | C (⅓ $Al^{3+}$), mmol/100 g of soil | | Discrepancy between the results with XO and arsenazo I,% |
|---|---|---|---|---|---|
| | | | XO | Arsenazo I | |
| Swamp soil No.1 | 5.58 ± 0.14 | 34.5 ± 3.5 | < 0.05 | < 0.025 | - |
| Swamp soil No.2 | 6.08 ± 0.14 | 4.3 ± 0.4 | < 0.05 | < 0.025 | - |
| Forest soil | 4.15 ± 0.14 | 2.6 ± 0.3 | 0.15 | 0.18 | 20 |
| Sod-podzolic soil | 4.29 ± 0.14 | 3.4 ± 0.3 | 0.06 | 0.08 | 33 |
| Clay soil | 4.07 ± 0.14 | 0.3 ± 0.1 | 0.19 | 0.23 | 21 |
| Sandy soil | 4.39 ± 0.14 | < 0.10 | 0.06 | 0.09 | 50 |

It can be seen that in swamp soils with a high humus content, the obtained aluminum concentration values are significantly lower than those for other types of soils, which can be explained by its binding into humic complexes. As follows from the data in the table, the determination error is influenced by the metabolic acidity: the higher the pH of the soil extract, the greater the determination error. This is due to the fact that the soluble form of aluminum prevails in acidic soils, and in soils close to neutral, aluminum is in the form of organomineral complexes and, as a result, the value of the content of the mobile form decreases.

With relatively small amounts of humus, it was not possible to identify a clear nature of its influence on the results of the analysis, however, the error of determination in all cases is greater than prescribed in the certified methodology.

To confirm that humus in low concentrations does not significantly affect the results of the analysis, the aluminum content in the filtrates of soil extracts with additives of a standard aluminum solution was determined. Figures 3-4 show diagrams reflecting a comparison of the errors in the determination of aluminum with XO and arsenaso I.

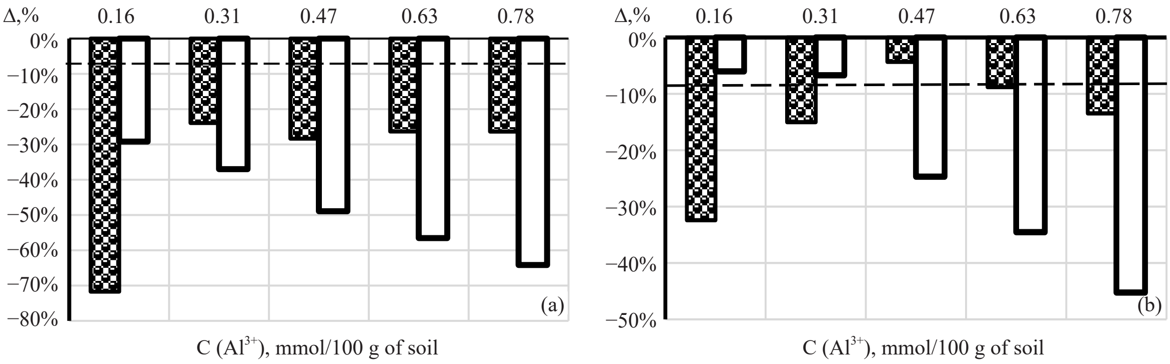


**Figure 3.** Results of determination of aluminum content in filtrates of extracts of swamp soils $C_0$ ($Al^{3+}$) < 0.05 mmol/100 g of soil with additives of the standard solution (□-in the presence of arsenazo I; ▩-with the help of XO); ▬ ▬ ▬ -the error value of the certified methodology using xylene orange (7.5%) (a) $pH_{KCl}$ = (5.58 ± 0.14) pH units, $C_{humus}$ = (34.5 ± 3.5)%; (b) $pH_{KCl}$ = (6.08 ± 0.14) pH units, $C_{humus}$ = (4.3 ± 0.4)%

Figure 3 shows the results obtained in the analysis of swamp soils that are close to neutral, with different humus content. The concentration of the determined component in these soils is lower than the minimum limit established by the certified methodology (< 0.05 mmol/100 g of soil).

From the diagrams shown in Figure 3, it can be concluded that the degree of humusification significantly affects the obtained values of aluminum content, both in the presence of xylene orange (according to GOST 26485) and using the developed algorithm with arsenase I. With a high humus content (Figure 3a), there is a significant excess of the error established by the certified methodology in the entire range of studied concentrations of additives of the component being determined. A decrease in the humus content (Figure 3b) leads to the fact that when analyzing a part of the studied samples with different additives, results were obtained that meet the accuracy requirements of the certified methodology.[9-11]

When determining the concentration of mobile aluminum using arsenazo I, a direct proportional change in the error of determination from the concentration of the additive was revealed, which indicates the possibility of introducing systematic corrections to the results of the analysis of real objects.

Figure 4 shows the results obtained in the analysis of highly acidic soils of various genesis, with a humus content differing by 10 times, with a concentration of the detectable component at the level of 0.2-0.3 mmol/100 g of soil. Similarly to the previously reported results, it was revealed that the degree of humusification significantly affects the obtained values of the aluminum content with the two studied reagents.

With a high humus content (Figure 4a), there is an underestimation of the results exceeding the permissible limits.

For concentrations obtained in the presence of xylene orange, the underestimation is more significant. It was revealed that a decrease in the humus content (Figure 4b) has a different effect on the results of the determination of mobile aluminum in the presence of xylene orange and arsenazo I.

The determination according to GOST 26485 leads to underestimated results up to an additive concentration of 0.3 mmol/100 g of soil and overestimated values-at the additive concentrations above 0.5 mmol/100 g of soil. When using arsenazo I, the values of the content of mobile Al were obtained that exceed the theoretically calculated values in the case of low concentrations of the additive (< 0.5 mmol/100 g of soil), and at higher values of the additive, the established values fall within the error range of the certified methodology. In this case, the results showed a proportional change in the error of determination from the concentration of the additive in the presence of the two studied indicators. This indicates the possibility of introducing systematic corrections to the results of the analysis of real objects obtained in the presence of arsenazo I and xylene orange.[12]

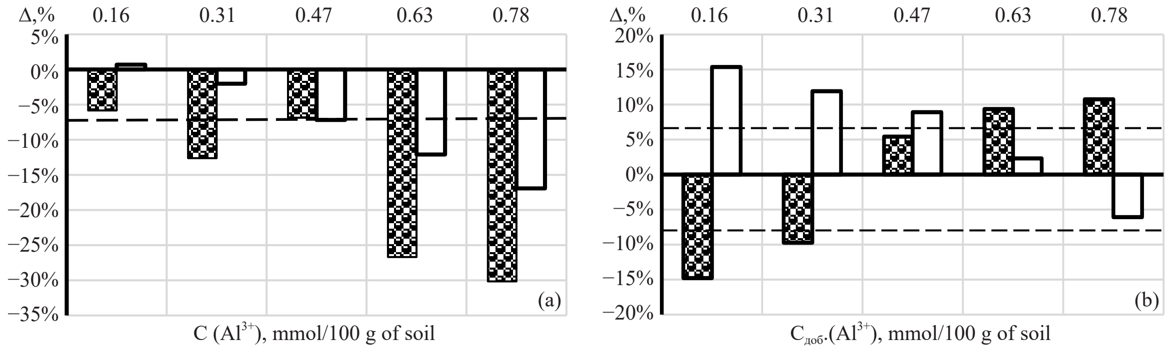


**Figure 4.** The results of determining the aluminum content in the filtrates of extracts of strongly acidic soils with additives of a standard solution (□-in the presence of arsenazo I; ▩-with the help of XO); — — —-the error value of the certified methodology using xylene orange (7.5%) (a) forest soil $C_0(Al^{3+})$ = (0.21 ± 0.02) mmol/100 g of soil, $pH_{KCl}$ = (4.15 ± 0.14) pH units, $C_{humus}$ = (2.6 ± 0.3)%; (b) clay soil $C_0(Al^{3+})$ = (0.27 ± 0.02) mmol/100 g of soil, $pH_{KCl}$ = (4.07 ± 0.14) pH units, $C_{humus}$ = (0.3 ± 0.1)%

To assess the effect of humus content on the results of the analysis of aluminum content at its low contents ((0.06 ± 0.02) mmol/100 g of soil), two native samples of highly acidic soils were analyzed:

1) sod-podzolic soil with the acidity of salt extract $pH_{KCl}$ = (4.29 ± 0.14) pH units and with the humus content equal to (3.4 ± 0.3)%;

2) clay soil-$pH_{KCl}$ = (4.39 ± 0.14) pH units and with a humus content below the lower limit of the certified procedure GOST 26213(< 0.15%).

It is noted that, regardless of the content of the humus, the results of the studied samples with different aluminum additives meet the requirements for the accuracy of the results regulated by the certified methodology (Δ = 30%), and the maximum deviation of the obtained values from the calculated values for arsenazo I does not exceed 17%, while for xylene orange it is the value of 24%.

The results of the study are in good agreement with the data presented by Morev et al.,[13] where the photometric method using arsenazo I was chosen as an arbitration method, and with the conclusions by Kyzyurova,[14] which indicates underestimated results obtained in the presence of reagents provided by GOST 26485-85, as well as their insufficient accuracy.

## 4. Findings

Thus, the possibility of using arsenazo I as a reagent for the spectrophotometric determination of exchangeable (mobile) aluminum in soils has been shown.

An algorithm for determination has been developed, tested on the standard solution of aluminum(III), and the comparative analysis of the determination of mobile aluminum in native soil samples according to the certified method and the experimental method with arsenazo I were carried out.

The effect of humus content on the results of the determination of mobile aluminum by the method with arsenazo I has been studied, it has been shown that humus has an effect only when its contents are high.

It is shown that the use of the indicator is possible with the introduction of systematic corrections to the results of the analysis of humusificated soils. A number of advantages of the proposed reagent have been established in comparison with the one provided for by the certified method, namely, obtaining more accurate results at high humus contents and a less lengthy analysis procedure.

The corresponding effect of the metabolic acidity of the soil has been established, and it is shown that the application of the developed algorithm is most effective in the analysis of acidic soils.

(1) The possibility of using arsenazo I as a reagent for the spectrophotometric determination of exchangeable (mobile) aluminum in soils has been shown.

(2) The determination algorithm has been developed, tested on a standard solution of aluminum(III). The comparative analysis of the determination of mobile aluminum in full-scale soil samples using a certified method and an

experimental method with arsenaso I has been carried out.

## Conflict of interest

The authors declare no conflict of interest.

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