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THE USE OF E-pH TERNARY DIAGRAMS IN SELECTING  
EXTRACTANTS OF AMORPHOUS IRON AND ALUMINIUM  
COMPOUNDS IN SPODIC SOILS IN ROMANIA

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INTRODUCTION

Iron humus podzols, acid soils with low biological activity, developed in a humid temperate climate, in forest and alpine zones, on acid parent materials, are characterized by the presence of colloid gels formed by the hydration and polymerization of Fe and Al oxides.

These have resulted from the chemical weathering of silicates maintained for a long time in an amorphous state in acid conditions by the organic matter which plays the role of a protection colloid or complexing agent, favouring the formation of amorphous, organo-mineral "complexes", as micellar associations. The quantity and distribution of this active amorphous material [7] in the soil profile are specific to the evolution stages of the present podzolization process [22].

For the study of amorphous soil material many methods of differential solubilization have been used on a simplifying hypothesis concerning the particle size, hydration degree, temperature, contact period etc. factors which can influence the kinetics of extraction reactions.

Due to the fact that the extraction based upon differential solubilization is the only way used in practice for separating the amorphous material — the elements dosed in extractants being of various origin, from hydrosoluble forms, complexed ions and gels associated with organic molecules or crystallized minerals to products of the partial attack of crystallized minerals — in order to ensure a correct interpretation of analytical data it is required to find an objective criterion for appreciating the selectivity of extractants, according to the chemical form of different elements separated from soils.

Thus, the elaboration of the E-pH diagrams for ternary systems, element-water-ligand, had conducted to the outlining of the first objective

criterion for appreciating the selectivity of extractants used in soil analysis [23].

Being a condensed, logical, generally admitted form of presenting the data characterizing the equilibrium conditions of simultaneous chemical and electrochemical reactions within the limits admitted for standard chemical potentials of components participating in the reactions considered, the E-pH diagrams have been elaborated by Pourbaix [18] for the majority of binary element-water systems. Over the last 15 years, binary diagrams have been used in soil science for studying hydromorphic soils. Bonneau et al. [1] recommends the Fe-water and Mn-water binary diagrams for the study of the solubility and mobility of these elements in soils.

The introduction into the element-water binary systems of a third constituent which can form complexes or insoluble salts, called for the elaboration of element-water-ligand ternary system diagrams, representing modifications of those of the binary systems that present the stability conditions of the respective dissolved or solid compounds [11—16].

The diagrams of the ternary systems permitted the extension of their applicability on to soil chemistry, as a first objective criterion for appreciating the selectivity of the extractants used in soil analysis [28].

The paper presents the E-pH equilibrium diagrams of the Fe-water-ligand (extractant) and Al-water-ligand (extractant) ternary systems, corroborated with the experimental results and their use as thermodynamical basis for proving the validity of the indexes established for the identification and characterization of the evolution stages of spodic soils [2, 21, 22].

#### METHODS

In elaborating the diagrams of the ternary systems some simplifying hypotheses have been advanced: the thermodynamic soil system is considered as a simply (Fe, Al)-water binary system, the kinetics of chemical reactions specific for the practical conditions in which selective extractions are made, as well as the reactivity difference of different soil Fe and Al forms (ionic forms, amorphous hydroxides, oxohydroxions with different polymerization degrees complexed or uncomplexed by the organic matter, crystallized hydroxides and oxides) have not been taken into consideration.

The main extractants recommended in soil science literature for extracting free (nonsilicate) forms of Fe and Al (associations of acids with a complexing action and a reducing agent, the latter not being taken into consideration) have been studied from the thermodynamic and experimental points of view [28, 29]. These extractants are: sodium pyrophosphate 0.1 M at pH 10 (P) — Duchaufour and Jacquin [5]; sodium

pyrophosphate 0.2 M at pH 7.3 with sodium dithionite (P-D) — Franzenmeyer et al. [7]; sodium citrate 0.2 M at pH 7.3 with sodium dithionite (C-D) — De Coninck et al. [3] modified by Vasu [21]; oxalic acid 0.4 M — ammonium oxalate buffered at pH 3.5 with sodium dithionite (O-D) — Duchaufour and Souchier [6] and, for Al, sodium hydroxide 0.5 M — Hashimoto and Jackson [9].

The E-pH ternary diagrams of Fe(Al)-ligand (pyrophosphate, citrate, oxalate)-HOH systems have been calculated and plotted taking into consideration the chemical and electrochemical reactions which can take place when Fe(Al) — especially the amorphous hydroxides and oxohydroxoions respectively, the components for which the selectivity of extractants is considered — are in the presence of the ligand. Thus, the thermodynamic conditions of the relative predominance of the components which can be formed in the respective systems, are established as well as their evolution as a function of the concentration in which they occur.

In order to facilitate the comparison of the diagrams, the concentrations of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  have been maintained constant in the system — for  $\text{Fe}^{3+}$  0.015 mol.l<sup>-1</sup> and for  $\text{Al}^{3+}$  0.01 mol.l<sup>-1</sup>. These correspond to the experimental conditions, expressed at 100 g soil: 1.5% Fe extracted with P solution, 2.3% Fe and 1.2% Al extracted with P-D solution, 3.8% Fe and 1.2% Al with C-D solution, 4.2% Fe and 1.35% Al with O-D solution and 2.7% Al with NaOH solution.

The highest stability of the complexes formed with different ligands (extractants) is about pH  $\pm$  1 units corresponding to the middle of the stability area of the complex formed by the action of the extractant (complexing agent) upon the studied element.

## RESULTS AND DISCUSSION

The analysis of superposed Fe-water-ligand (extractants) diagrams shows the following (Fig. 1): sodium pyrophosphate at pH 10 can extract the smallest amounts of Fe, predominantly corresponding to the organo-mineral compounds (a conclusion also emphasized by comparing the amounts of C extracted by P or by P-D, which are practically the same); pyrophosphate-dithionite at pH 7.3 can extract somewhat larger amounts, predominantly corresponding to the active amorphous Fe compounds (ionic forms, amorphous hydroxides, oxohydroxoions with different polymerization degrees — recent gels, maintained in this form in acid medium by the organic matter having a protection colloid or complexing agent role); dithionite-oxalic buffer and dithionite-citrate can extract the largest amount of Fe, including, besides the ionic and amorphous forms, cryptocrystalline forms, as well as crystallized hydroxides and oxides.

Besides the selectivity of the extractants studied comparatively the E-pH ternary diagrams show the uselessness of adding the natrium dithionite as a reducing agent to the extracting solutions. The stability limits of the complexes formed with  $\text{Fe}^{3+}$  and their compounds drop much lower than 1/2 in the stability area of  $\text{Fe}^{2+}$  from the diagrams of the Fe-HOH system, especially when the oxalic buffer is concerned.

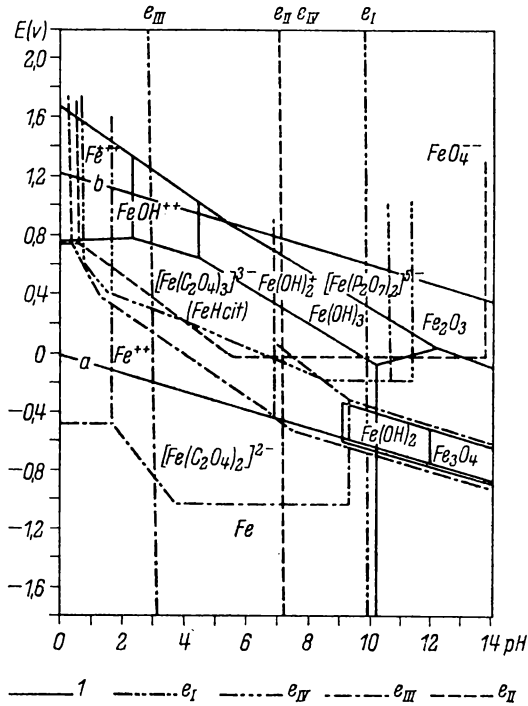


Fig. 1. Equilibrium diagrams E—pH of systems  
 1 — Fe-HOH,  $e_I$  — Fe-HOH pyrophosphate 0,1 M,  $e_{IV}$  — Fe-HOH pyrophosphate 0,2 M,  
 $e_{III}$  — Fe-HOH oxalate,  $e_{II}$  — Fe-HOH citrate

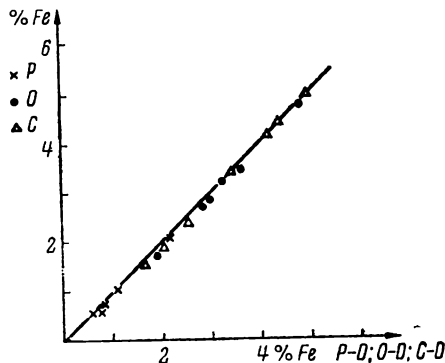


Fig. 1a. Fe extracted with or without dithionite in cambic, spodic and andic soils

In chemical literature no complexes of  $\text{Fe}^{2+}$  with the complexing agents (extractants), excepting citrate, are taken into consideration. The experimental results of extractions with or without adding dithionite confirm the conclusions deduced thermodynamically (Fig. 1a).

The analysis of the superposed Al-water-ligand (extractant) and Al-water diagrams (Fig. 2) shows that dithionite-citrate at pH 7.3 extracts predominantly active amorphous Al. Because for sodium pyrophosphate

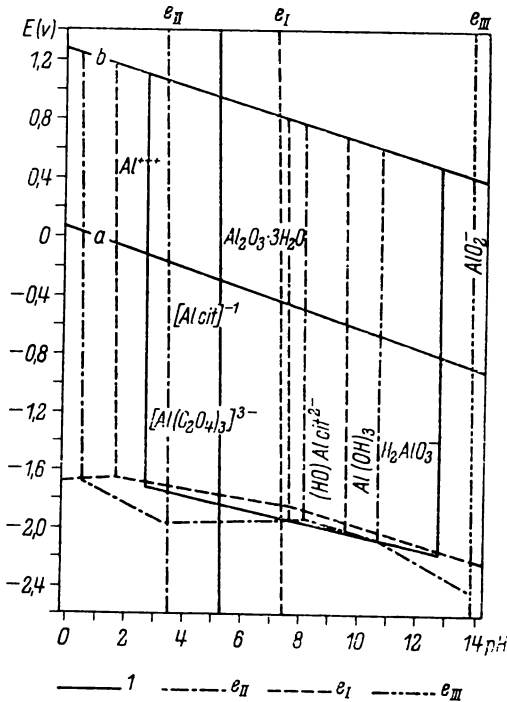


Fig. 2. Equilibrium diagrams E-pH of systems  
 1 — Al-HOH,  $e_{II}$  — Al-HOH oxalate,  $e_I$  Al-HOH citrate,  $e_{III}$  — Al-HOH-NaOH

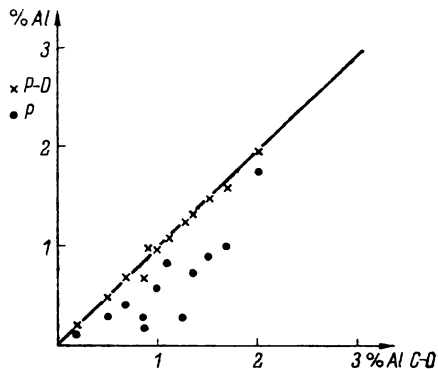


Fig. 2a. Active amorphous Al in cambic, spodic and andic soils

the constants of the Al complex are not mentioned in chemical literature, a comparison of the experimental results with those obtained for citrate-dithionite has been resorted to. It has become evident that sodium pyrophosphate at pH 10 can extract somewhat lower amounts than citrate-dithionite at pH 7.3, probably the Al form the organo-mineral compounds (the C amounts extracted by P and P-D are practically identical); the fact that pyrophosphate-dithionite at pH 7.3 extracts amounts of Al identical with those extracted by C-D (Fig. 2a) and the indirect evidence given by Franzmayer et al. [7] enables us to infer that P-D extracts

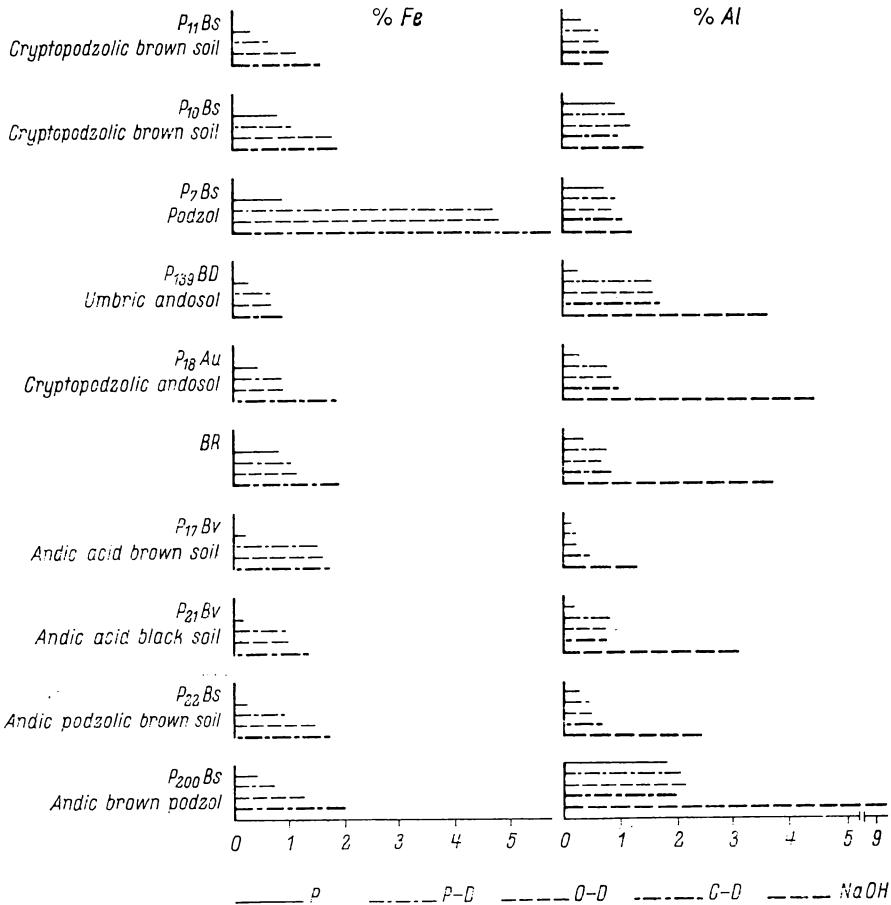


Fig. 3. Fe, Al quantities extracted with different extractants from representative cambic, spodic and andic soils

predominantly active amorphous Al. The oxalic-dithionite buffer can extract larger Al amounts, namely predominantly active amorphous Al and aged gels; sodium hydroxide 0.5 M solution extracts total amorphous Al and cryptocrystalline forms (including the compounds of the allophanic type), as well as slightly crystallized silicates (having different ordina-

tion degrees) of the halloizit and methahalloizit type [8], a fact also confirmed by Hétier [10].

The experimental results obtained on Mount Fägåraş spodic soils evolved on chlorit-sericite schists under beech, beech mixed with conifers, spruce or meadows, at 650—2240 m a.s.l. with an annual average rainfall of 750—1250 mm and an annual average temperature of 7 to —1.2°C and Mount Harghita spodic and cambic soils of andic character evolved on andezites with pyroxens under conifers mixed with beech, spruce or meadows, at 950—1750 m a.s.l. with an annual average rainfall of 730—1300 mm and an annual average temperature of 1.5 to 5°C, confirm the practical validity of the suppositions deduced thermodynamically (Fig. 3). This attests the accuracy of the interpretation of E-pH diagrams of the Fe(Al)-ligand ternary systems as an objective criterion for the selectivity of the extractants, for which only indirect evidence has been available [24] up to the present.

Thus, it is proved that the hypothesis used over the last 12 years is valid, namely that the P-D or P solution extracts predominantly active amorphous Fe and Al, these being the specific constituents of the contemporary iron-humus illuvial process. The spodic character is estimated by the corroboration of morphological soil features with the limits concerning the active amorphous Fe and Al amounts and dynamics (expressed by the maximum value of the soil and, within the same limits, to the nature of parent material (Table 1).

The mentioned criteria have been also compared with both criteria given in soil Taxonomy, one for identifying the spodosols and the other for the spodic character of andosols, which cannot be used in estimating

Table 1

Specific values and variability indexes for active amorphous material  
in spodic and cambic soils /comparison term/

Soil subtype	Fe %	Al %	$\frac{Fe+Al+C}{\text{clay}}$	Maximum $I_v^x$			
				Fe	Al	Fe+Al	$\frac{Fe+Al+C}{\text{clay}}$
Acid brown soil	0.4-0.8	0.1-0.4	<0.15 0.04-0.10	1.1-1.3	1.1-1.3	1.1-1.6	1.0-1.4
Cryptopodzolic brown soils	0.5-1.0	0.3-1.0	>0.15 0.16-0.52	1.1-2.5	1.4-2.2	1.3-1.9	1.4-2.0
Podzolic brown soils	0.4-1.7	0.3-0.8	>0.15 0.21-0.62	1.6-2.3	1.3-2.0	1.2-1.8	1.4-2.0
Brown podzols	0.2-2.0	0.2-1.0	>0.15 0.27-1.00	1.5-4.0	2.0-5.0	1.8-3.3	2.1-3.0
Podzols	0.5-5.0	0.04-1.8	>0.15 0.40-1.00	>4.1 4.1-50	>4.5 4.5-20	>3.4 3.3-25	>3.1 3.1-15

$x - I_v$  - variability index: ratio of specific values for each horizon to the minimum values for eluviated horizons; O and BD horizons are not taken into consideration.

the evolution stages of spodosols (Guide Book of National Conference for Soil Science — Braşov, 1979).

The experimental results accumulated have confirmed the validity of the established indexes. Over the last 12 years of comparative studies of spodic, cambic, argillic and andic soils more than 100 soil profiles have been analyzed from the point of view of the amounts and dynamics of different Fe, Al and free Si forms. These soils have been developed on various crystalline schists, sandstones, conglomerate, marls, limestones, andesites and pyroclastites, under beech, beech mixed with conifers, spruce and meadows, in the Southern and Eastern Carpathians, at of 600—2240 m a.s.l., an annual average rainfall of 700—1250 mm and an annual temperatures of 8 to  $-2^{\circ}\text{C}$  [2, 21, 22, 25]. The results have been confirmed also by other studies carried out in Romania and abroad [4, 17, 20]. Moreover, these results have proved that the criteria established on the basis of active amorphous material dynamics have a general validity not only for spodic soils with obvious spodic morphological features, as for instance podzolic brown soils, brown podzols and iron-humus podzols, but also for spodic soils with obscure spodic morphological features, such as the brown crypthopodzolic soils (with evolution stages similar to podzolic brown soils or even brown podzols), as well as for soils whose spodic character is superposed on the andic one [25] Fig. 4.

The examples given in Fig. 4 show the same dynamics of active amorphous materials, as expressive of the iron-humus podzolic process of spodosols developed on chlorite-sericitic schists, as for those developed on andezites with pyroxens<sup>1</sup>. For the former ones the only amorphous material, there occur aged gels and cryptocrystalline or crystalline transition podzolic process, while in the latter soils, besides the active amorphous material, there occur aged gels and cryptocrystalline or crystalline transitions with different ordination degrees, characteristic of the andic soil-forming process.

The recognition of Fe and Al forms with the aid of E-pH diagrams, thus constitutes an objective argument for identifying the chemical constituents characteristic of different pedogenetic processes, even if they coexist as a result of soil evolution.

The recognition of Fe and Al also substantiates and confirms the validity of the research work on the role of amorphous materials in characterizing soil trophicity, for instance, as a source of pH dependent acidity [27], as an ecological determinant with a limitative role in spruce growth [26] or in phosphate adsorption [19].

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<sup>1</sup> The soils are described in the Guide Book of National Conference for Soil Science, Braşov, 1979.



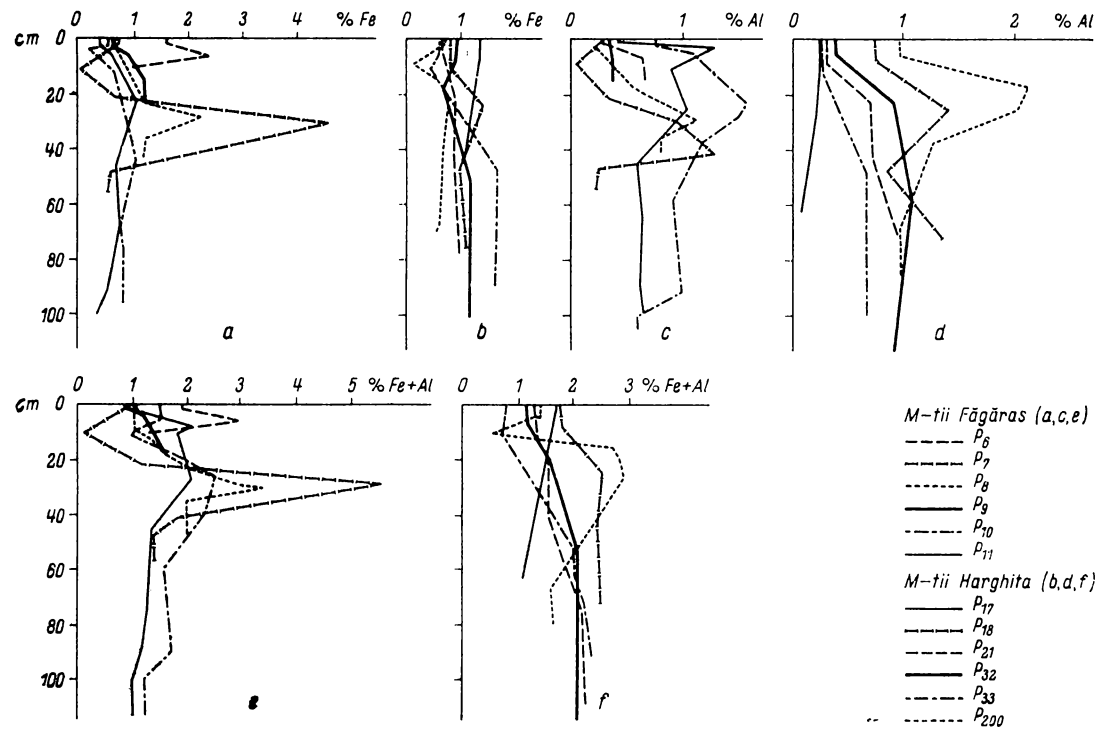


Fig. 4. Fe and Al dynamic in cambic, andic and spodic soils

P<sub>6</sub> — cryptopodzolic silicate soil, P<sub>7</sub> — podzol, P<sub>8</sub> — podzolic brown soil, P<sub>9</sub> — podzolic brown soil, P<sub>10</sub> — cryptopodzolic brown soil, P<sub>11</sub> — cryptopodzolic brown soil, P<sub>17</sub> — andic acid brown soil. P<sub>18</sub> — cryptopodzolic andosol, P<sub>21</sub> — andic acid black soil, P<sub>32</sub> — andic podzolic brown soil, P<sub>33</sub> — andic podzolic brown soil, P<sub>200</sub> — andic brown podzol.

## CONCLUSIONS

In conclusion, the E-pH ternary diagrams, used as an objective criterion for selecting extractants, provide a real physical sense for the analytical results obtained by conventional methods. Consequently, they also ensure the validity of their interpretation in soil systematics, as well as in estimating soil production capacity. By comparing the data on the chemical forms of nutrients obtained in this way with phytophysiological studies the diagrams can be also used in future for establishing new methods of soil analysis as well as for studying soil-plant relationships.

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ПРИМЕНЕНИЕ ТРЕХКОМПОНЕНТНЫХ ДИАГРАММ E-pH ПРИ ОТБОРЕ РАСТВОРИТЕЛЕЙ АМОРФНЫХ СОЕДИНЕНИЙ ЖЕЛЕЗА И АЛЮМИНИЯ В СПОДИКОВЫХ ПОЧВАХ РУМЫНИИ

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Резюме

В статье представлена возможность использования трехкомпонентных диаграмм типа элемент-вода-лиганд и двухкомпонентных типа элемент-вода для установления предела относительного преобладания в почвенном экстракте определенных соединений железа

и алюминия. На диаграммах проанализированы двухкомпонентные системы Fe(Al) вода и трехкомпонентные Fe-вода-лиганд (пирофосфат, цитрат, оксалат), Al-вода-лиганд (цитрат, оксалат), а также Al-вода-гидроокись натрия. Результаты проведенных исследований подтвердили пригодность разработанных диаграмм для подбора самых благоприятных условий экстракции и, вопреки предписаниям некоторых авторов, показали ненужность добавления дитионита в экстракционные растворы при извлечении из почвы несиликатных форм железа и алюминия. Использование диаграмм и соответствующий подбор условий экстракции дают возможность установить химические критерии, позволяющие объективно разграничить криптоподзолистые, подзолисторжавые, ржаво-подзолистые и подзолистые почвы, а также почвы, в которых процессы подзолообразования сильно маскируются другими процессами (нпр. почвы с признаками андосолей).

Подчеркивается роль аморфных веществ в формировании трофических свойств почв.

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## ZASTOSOWANIE TRÓJSKŁADNIKOWYCH DIAGRAMÓW E-pH PRZY WYBORZE EKSTRAHENTÓW AMORFICZNYCH ZWIĄZKÓW ŻELAZA I GLINU W SPODIKOWYCH GLEBACH RUMUNII

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### Streszczenie

Przedstawiono możliwość wykorzystania diagramów trójskładnikowych typu pierwiastek—woda—ligand i dwuskładnikowych typu pierwiastek—woda do ustalenia zakresów względnej dominacji w ekstrakcie glebowym określonych związków żelaza i glinu. Na diagramach przeanalizowano układy dwuskładnikowe Fe(Al) — woda oraz trójskładnikowe Fe-woda-ligand (pирофосфоран, cytrynian, szczawian) i Al-woda-ligand (cytranian, szczawian), a także Al-woda-wodorotlenek sodu. Wyniki przeprowadzonych badań potwierdziły przydatność opracowanych diagramów do wyboru najodpowiedniejszych warunków ekstrakcji i wbrew zaleceniom niektórych autorów wykazały zbędność dodawania podsiarczynu (dithionitu) do roztworów ekstrakcyjnych przy wydzielaniu z gleby niekrzemianowych form żelaza i glinu.

Korzystając z diagramów i odpowiednio dobierając warunki ekstrakcji uzyskano możliwość ustalenia chemicznych kryteriów pozwalających na obiektywne rozgraniczenie gleb skrytobielicowych, bielicowo-rdzawych, rdzawo-bielicowych i bielic, a także gleb, w których procesy bielicowania są silnie maskowane przez inne procesy (na przykład gleby z cechami andosoli).

Podkreślono rolę substancji bezpostaciowych w kształtowaniu troficzności gleb.

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