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THE SOLUBILITY OF MICRONUTRIENTS IN AMMONIUM POLYPHOSPHATE SOLUTIONS

S. Górn-Nagy*, P. Káldi**, Mrs. J. Bésán*** and A. Szántó***

(* Committee of National Technical Development, Budapest;
** Department of Chemical Technology,
Veszprém University of Chemical Engineering, Veszprém;
*** Research Institute for Heavy Chemical Industries, Veszprém)

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Experiments were carried out to determine the solubilities of micronutrients [Fe(III), B, Zn, Cu, Mn, Co, Mo] in 10—34—0 ammonium polyphosphate solution. As a result a method was elaborated which, in the case of polyphosphate solutions containing three of the above mentioned micronutrients, enables the calculation of concentration relationships without the knowledge of the composition and stability coefficients of the formed complex compounds. This method can be extended to the description of fertilizer solutions containing more than three micronutrients.

1. Introduction and Literature

Those elements are termed micronutrients which take part in the structure of a plant's organism and which are present there in a concentration of less than 10^{-2} wt. per cent. These elements, although their amount is more or less negligible, play an important role in the life of a plant. The most important micronutrients are: iron, boron, zinc, copper, manganese, cobalt and molybdenum.

In a modern rural economy which applies industrial monocultural production methods, the need for micronutrients increases every day. The applied production technologies consume steadily growing amounts of NPK fertilizers and, as a consequence the amount of harvested products of a given region, constantly increases. The result of experiments, carried out with different types of fertilizers, show that a further increase of macronutrients results in a lower increase of products from a soil properly supplied with nitrogen, phosphorous and potassium, but with the rise in the micronutrient concentration of the land, the result is a marked growth of the harvested product. Therefore in countries with a developed agriculture a demand arises for supplying the micronutrient deficiency of the soils in addition to and together with fertilization of different nitrogen, phosphorous and potassium compounds.

Based on the data that has appeared in literature, the supplement of micronutrients can easily be solved with the aid of liquid fertilizers, among these the polyphosphate solutions have the advantage that they dissolve the inorganic salts until a degree determined by their original polyphosphate concentration [1a]—[14].

In *Table 1*, the solubility data of micronutrients are presented, related to NP solution containing 8-24-0 (ortophosphate solution); 10-34-0 (40—45 wt. per cent polyphosphate solution) and 11-37-0 (60—70 wt. per cent polyphosphate solution) macronutrient ratios and having only one micronutrient compound. The numbers given above indicate the N-P_2O_5-K_2O concentration of the fertilizer solution, in wt. per cent [1a], [3], [4], [7]—[14].

Table 1.

The solubility of inorganic salts—micronutrients—in ammonium polyphosphate solutions
[1a], [3], [4], [7]—[14]

Dissolved salt	Solubility (%) of (Zn, Cu, Fe, Mn, B, Mo) in		
	8=24=0	10=34=0 solutions	11=37=0
ZnO	0.05	2.25	3.0
$ZnSO_4 \cdot H_2O$	0.05	1.50	2.0
$ZnCO_3$	0.05	2.25	3.0
CuO	0.03	0.53	0.7
$CuSO_4 \cdot 5\,H_2O$	0.13	1.13	1.5
$Fe_2(SO_4)_3 \cdot 9\,H_2O$	0.08	0.80	1.0
Mn_3O_4	< 0.02	0.15	0.2
MnO	< 0.02	—	0.2+
$MnSO_4 \cdot H_2O$	< 0.02	—	0.2+
$Na_2MoO_4 \cdot 2\,H_2O$	0.5++	0.38++	0.5++
$Na_2B_4O_7 \cdot 10\,H_2O$	0.90	0.90	0.9

Note:
+ precipitate formed after several days
++ highest concentration examined

The inorganic compounds of zinc, manganese, copper and iron are almost insoluble in ortophosphate solutions (their solubility is less than 0.1 wt. per cent) due to the formation of metal ammonium ortophosphates.

The relatively higher solubility of metal salts in solutions containing polyphosphates can be explained by the sequestering properties of the condensed phosphates. If a polyphosphate solution is poured progressively into a solution of multivalent metal ions, at first a precipitate forms which dissolves later in the presence of excess polyphosphate. All the condensed phosphates form insoluble salts with multivalent metal ions which transform into a soluble complex compound in the excess of polyphosphate. This phenomenon is termed sequestering property [15]. The sequestering property of the ammonium polyphosphate solution used for fertilizers is attributed to their dipolyphosphate and tripolyphosphate content.

The concentration of micronutrients dissolved in polyphosphate base fertilizer solutions is influenced by the solubility relationships of the other compounds present in the system. *In a system which is in equilibrium, the actual values of the metal ion concentrations are the results of the stability coefficients of complex forming reactions and the solubility relationships of the final products* [1b].

The structure of most of the complexes formed in polyphosphate solutions is unknown, only a few of them were examined thoroughly. Neither the numerical values of the stability coefficients nor the solubility products of these known complexes can be used for the determination of the maximum allowable metal concentration of polyphosphate solutions. These data were determined in pure systems, in dilute electrolytes and hence they cannot be related to the complex mixtures of fertilizer solutions.

In concentrated polyphosphate solutions, the concentration of micronutrient can be higher or lower compared to the previously mentioned data, due to the unknown equilibrium processes. A further complication arises that the form and the composition of the solid phases assumed by the solubility relationships are not always equal due to the crystal dimorphism and isomorph substitution, which have significant effects on the solubility. Adding mixtures of micronutrients to fertilizers, the isomorph substitution occurs more frequently in reaction products.

The large number of components made the generally used solubility diagrams inapplicable for the determination of solubility data and for the identification of solid phases [16]. The liquid polyphosphate solutions are too complicated systems to investigate or represent with simple phase diagrams.

The result of the mentioned difficulties is that the published data on micronutrient solubility in polyphosphate solutions are extremely rare and insufficient, up to now the concentration data of the single micronutrients in polyphosphate solutions are available, but the data concerning cobalt are missing.

Hitherto only two brief references were found dealing with multicomponent systems:

- Formaini stated [11] that the concentration of copper, zinc and manganese in a polyphosphate solution can be calculated with the weighted average of the single solubility data,
- based on Mortvedt's publication the micronutrient concentration limit of 3 wt. per cent cannot be exceeded and the storage time of liquid fertilizers containing various nutrients is shorter than those which contain only a single one [1a].

2. The Method Used for the Determination of Micronutrient Solubility

For the solution of the questions outlined above, a method was elaborated which can be applied for the determination of the solubility of micronutrient mixtures in polyphosphate solutions without the knowledge of the processes taking place during the dissolution and of the composition of the compounds formed.

In the following a method is discussed which can be applied in the case of solutions containing three micronutrients. The principle of the method can be extended to polyphosphate solutions containing more than three micronutrients, but in these cases the depiction in four, five or more dimensions is impossible. This method was elaborated for the determination of micronutrient solubility in ammonium polyphosphate fertilizers. It is conceivable that similar problems can be successfully if this method is applied.

As the first step, *the solubility data of the single micronutrient* was determined. The examined metal salt was poured into 100 g. of well mixed ammonium polyphosphate solution, at room temperature until an insoluble precipitate was formed. Then the solution was stirred for 24 hours and the precipitate was separated from the solution with an ultracentrifuge (5,000 to 6,000 rpm), and the micronutrient concentration of the clear solution was determined by an atomabsorption spectrometer. If the p_H value of the solution decreased during the dissolution of the salt, ammonia gas was bubbled into the solution.

The metal concentration value of the clear solution being in equilibrium with the formed precipitate was taken as the solubility of the examined salt.

Knowing the solubility data of the examined micronutrient salts, in the second step the *solubilities of micronutrient pairs* were determined. A series of solutions were prepared which contained 25, 50, 75 and 100 per cent of the soluble amount of the given salt and into these well mixed solutions was added the second salt, at room temperature, until the formation of an insoluble precipitate. Then, if necessary, the p_H value of the solutions was adjusted to 5.85. The following procedures were similar as described above.

The metal concentrations of polyphosphate solutions containing two micronutrients were presented with the help of a rectangular co-ordinate system, the solubilities of the single micronutrients were plotted on the axes in (g metal/100 g ammonium polyphosphate) [APP] units. The concentration values of the solution containing two micronutrients form a plane limited by the axes, this means that all points of this figure represent stable fertilizer solutions. The border curves of the plain figure were approximated by straight lines. This neglection could be done because the examined concentration range is very narrow and as a consequence, the curvature is negligible.

The following method was used for *the determination of the concentration relationships of polyphosphate solutions containing three micronutrients:*

The solubility relationships of three micronutrients can be represented by a figure having three dimensions i.e. by a solid. The construction of this solid is described below:

The plane figures determined by micronutrient pairs was placed into a space co-ordinate system. Here, the solubilities of the single micronutrients are given on the x, y and z axes as point values, and the planes formed by the axes represent the solubilities of micronutrient pairs. This is shown in *Fig. 1.*

Marking the tips of the solid with letters:

P_2 $(a, 0, 0)$
P_3 $(0, b, 0)$
P_4 $(0, 0, c)$
P_5 $(A, B, 0)$
P_6 $(C, 0, D)$
P_7 $(0, E, F)$

(It is to be noted that the origin, formed by the axes is meaningless!)

The co-ordinates of the points being in brackets, represent the solubilities of the individual metals or micronutrient pairs: P_2, P_3 and P_4 give information

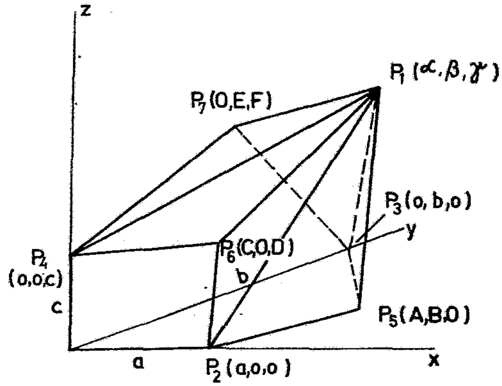

Fig. 1
The Solubility of Micronutrient Triad in General Case
a, b, c = the maximum metal concentration (g metal/100 g APP) of the system containing single micronutrient
A, B, C, D, E, F = the maximum metal concentration (g metal/100 g APP) of the system containing micronutrient pairs
α, β, γ = the maximum metal concentration (g metal/100 g APP) of the system containing micronutrient triad

about the concentration of the micronutrient, while points P_5, P_6 and P_7 represent the solubility relationships of micronutrient pairs. Marking an optional $P_1(\alpha, \beta, \beta)$ point—here α, β and γ give the solubility data of three micronutrients being present in the solution—and let us connect this together with the points P_2, P_3, P_4, P_5, P_6 and P_7. These latter points are carriers of certain information. Now, a plane can be placed on P_1 and on both the points being in neighbourhood of P_1; six such planes can be placed. In this way a solid can be formed which is bordered by planes representing the solubilities of the examined micronutrients. For the mathematical description of this solid the equation of a plane represented by three points can be used. Taking the symbols given in *Fig. 1:*

For the plain represented by P_1, P_2 and P_5:

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{A}{a}\right)+\frac{z}{\gamma}\left(1-\frac{\alpha}{a}-\frac{\beta}{B}+\frac{A}{a}\cdot\frac{\beta}{B}\right)=1$$

For the plain represented by P_1, P_3 and P_5:

$$\frac{x}{A}\left(1-\frac{B}{b}\right)+\frac{y}{b}+\frac{z}{\gamma}\left(1-\frac{\alpha}{A}-\frac{\beta}{b}+\frac{B}{b}\cdot\frac{\alpha}{A}\right)=1$$

For the plain represented by P_1, P_2 and P_6:

$$\frac{x}{a}+\frac{y}{\beta}\left(1-\frac{\alpha}{a}-\frac{\gamma}{D}+\frac{C}{a}\cdot\frac{\gamma}{D}\right)+\frac{z}{D}\left(1-\frac{C}{a}\right)=1$$

For the plain represented by P_1, P_4 and P_6:

$$\frac{x}{C}\left(1-\frac{D}{c}\right)+\frac{y}{\beta}\left(1-\frac{\alpha}{C}-\frac{\gamma}{c}+\frac{\alpha}{C}\cdot\frac{D}{c}\right)+\frac{z}{c}=1$$

For the plain represented by P_1, P_4 and P_7:

$$\frac{x}{\alpha}\left(1-\frac{\beta}{E}-\frac{\gamma}{c}+\frac{\beta}{E}\cdot\frac{F}{c}\right)+\frac{y}{E}\left(1-\frac{F}{c}\right)+\frac{z}{c}=1$$

For the plain represented by P_1, P_3 and P_7:

$$\frac{x}{\alpha}\left(1-\frac{\beta}{b}-\frac{\gamma}{F}+\frac{\alpha}{F}\cdot\frac{E}{b}\right)+\frac{y}{b}+\frac{z}{F}\left(1-\frac{E}{b}\right)=1$$

Dealing with the examination of three given metals, the values of a, b, c, A, B, C, D, E and F are known from the previously discussed experiments. The task is now the determination of the place of point P_1. Knowing the solubility relationships of the given micronutrient pairs, the form of the solid is generally simpler as it is depicted in *Fig. 1.* During the determination of the data representing the solid which describes the concentration relationships of three micronutrients, the aim is to prove that those solutions are stable which can be characterized by the concentration values being "inside" the solid.

For clarity *Fig. 2* shows the photograph of the solid fabricated from wire.

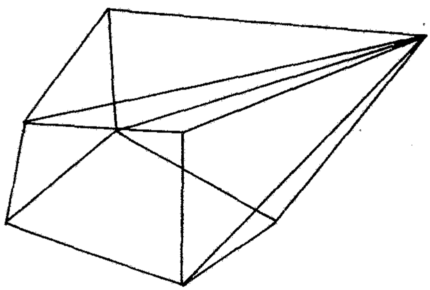

Fig. 2
The Solid Representing the Solubility Relationships of Micronutrient Triad

3. Experimental Results

The application of the method discussed above is shown by the solubility determination of micronutrients in 10-34-0 ammonium polyphosphate solution.

The 10-34-0 polyphosphate solution was prepared in the laboratory. Its analysis data are as follows:

$$N = 9.58 \text{ wt. per cent}$$
$$P_2O_5 = 34.00 \text{ wt. per cent}$$

The distribution of the total P_2O_5:

ortophosphate	52.3	per cent
diphosphate	41.9	per cent
triphosphate	5.7	per cent

$$\text{Density} = 1.3488 \text{ g/cm}^3$$
$$p_H = 5.85$$

The used inorganic compounds—or micronutrients—and their metal concentrations are listed in *Table 2.*

Table 2.

Compounds used as micronutrient source

Micronutrient	Compound		
	name	formula	metal content %
Boron	Borax	$Na_2B_4O_7 \cdot 10\ H_2O$	11.40
Molybdenum	Ammonium Molybdenate tetrahydrate	$(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$	54.40
Zinc	Zinc Sulphate heptahydrate	$ZnSO_4 \cdot 7\ H_2O$	22.85
	Zinc Oxide	ZnO	80.85
Copper	Copper Sulphate pentahydrate	$CuSO_4 \cdot 5\ H_2O$	25.50
Manganese	Manganous Sulphate monohydrate	$MnSO_4 \cdot H_2O$	32.50
Cobalt	Cobaltous Nitrate monohydrate	$Co(NO_3)_2 \cdot H_2O$	31.08
Iron	Ferric Ammonium Sulphate	$Fe(NH_4)(SO_4) \cdot 12\ H_2O$	11.6

The solubilities of the single micronutrients are presented by the numerical values of a and b, in *Table 3.*

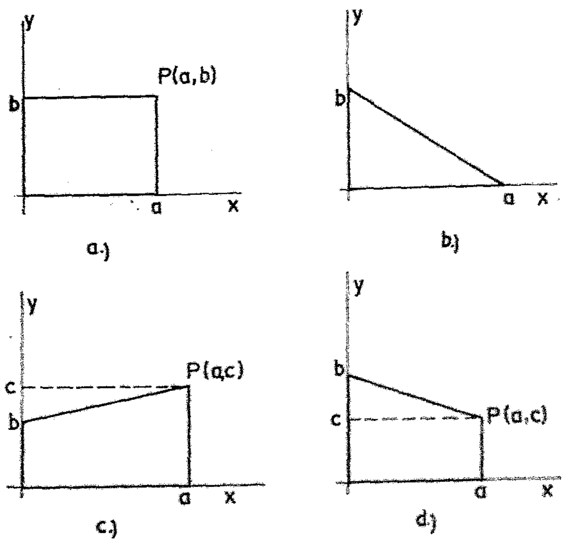

Fig. 3

Diagrams Describing the Concentration Relationships of Micronutrient Pairs in 10-34-0 Ammonium Polyphosphate Solution

Table 3.

The solubility of micronutrient pairs in 10=34=0 ammonium polyphosphate solution (see *Fig. 3*)

Micronutrient pair	Type of diagram	Solubility g metal/100 g APP. Symbols used in *Fig. 3*		
		a	b	c
B-Mo	3a	1.75	1.00	—
B-Zn	3a	1.75	2.08	—
B-Cu	3a	1.75	1.30	—
B-Fe	3c	1.75	2.70	3.66
B-Co	3c	1.75	0.34	1.00
B-Mn	3d	1.75	0.07	0.03
Mo-Zn	3a	1.00	2.08	—
Mo-Cu	3a	1.00	1.30	—
Mo-Fe	3a	1.00	2.70	—
Mo-Co	3a	1.00	0.34	—
Mo-Mn	3a	1.00	0.07	—
Cu-Zn	3b	1.30	2.08	—
Cu-Mn	3b	1.30	0.07	—
Cu-Co	3c	1.30	0.34	0.67
Zn-Mn	3b	2.08	0.07	—
Zn-Co	3b	2.08	0.34	—
Fe-Cu	3a	2.70	1.30	—
Fe-Zn	3b	2.70	2.08	—
Fe-Mn	3a	2.70	0.07	—
Fe-Co	3c	2.70	0.34	0.67
Co-Mn	3b	0.34	0.07	—

Table 3 and *Fig. 3* show the solubility relationships of micronutrient pairs. As micronutrients Fe(III), B, Zn, Cu, Mn, Co and Mo were selected and the solubility of the given micronutrient pairs, determined by the method described above, can be presented by one of the diagrams given in *Fig. 3*.

The solubility data of the micronutrient pairs were substituted into the general equation system of the solid depicted in *Fig. 1* and as a result the configuration given in *Fig. 4* was gained which describes the *solubility relationships of the micronutrient triad.*

Knowing these solids the method was selected, using this it could be proved with relatively few experiments that the solutions characterized by the component concentrations which are "inside" the constructed solid are stable and no precipitate forms. In the case of solutions by which the concentration data of the micronutrient components are "outside" the body, a precipitate forms.

The method used was as follows:

In the cases of *a, b, c, d, e* and *f* of *Fig. 4/1*, the component concentrations were increased along the body diagonal, connecting together the point *P* and the origin. The aim was to reach the point *P*. If in this case the solution was

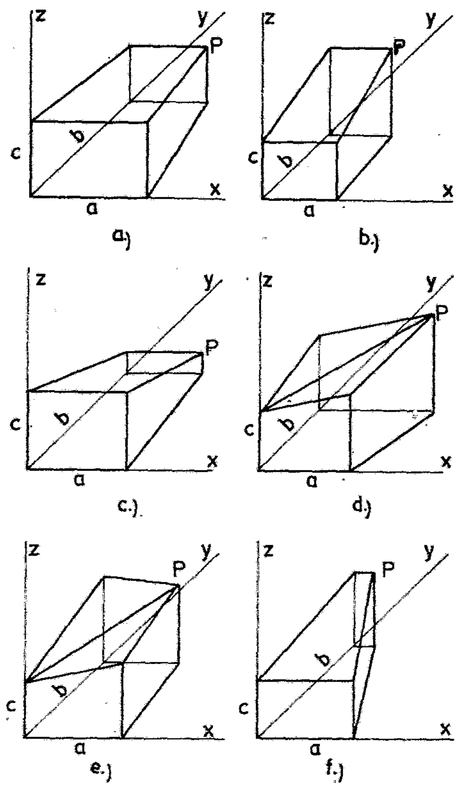

Fig. 4/1
Special Cases of the Solubility of Micronutrient Triads in 10=34=0 Ammonium Polyphosphate Solutions

stable, an attempt was made to "step out" from the formation i.e. more inorganic salts were added into the solution. If this experiment resulted in a precipitate formation, this verified the soundness of the presumption.

In the case of the triangle base prism shown in *Fig. 4/2* g, the increase of component concentration was carried out along the arrow which lies on the boundary plane, and a further increase of the concentration was attempted.

In the cases of *h*, *i*, *j*, *k*, *l* and *m* of *Fig. 4/2* the concentrations were similarly altered, the directions marked with arrows, until the point *P* was reached, taking the formations of *h*, *i* and *j* the samples characterized by A were also prepared.

If the p_H value of the solutions decreased due to the dissolution of the micronutrients, it was readjusted again with ammonia gas until the value of 5.85.

The numerical data of the solubility values of micronutrient triads are listed in *Table 4*. The representation of the micronutrient concentration on the *x*, *y* and *z* axes was carried out in the sequence given in the first column of the *Table*, i.e. the α co-ordinate of point *P* gives the first, β the second and γ the

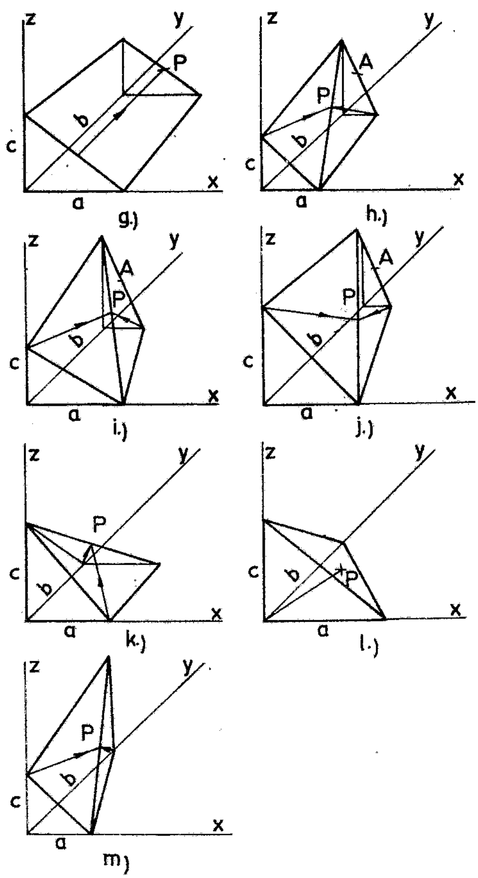

Fig. 4/2
Special Cases of the Solubility of Micronutrient Triads in 10=34=0 Ammonium Polyphosphate Solutions

third element concentration existing in the fertilizer solution characterized by point *P*. The section of the three axes (a, b, c) is the solubility of the given metal salt, and the three planes of the spatial co-ordinate system being perpendicular to each other, the figures take place which describe the solubility of 2—2 micronutrients. The values of these were presented above and with their help the sizes of the solid can be calculated.

In the cases illustrated with *Figure 4/1 a—f*, the numerical values of the α, β and γ co-ordinates of point *P* are also presented in *Table 4* on the one hand, the cause of this is the prevention of uncertainties caused by the deforming effect of the drawings, and on the other hand the co-ordinates of the point marked with + symbol do not follow unequivocally from the solubility data of micronutrient pairs. In the cases of *Fig. 4/2 g—m*, the point *P* moves along one of the edges or on the surface of the solid, therefore their co-ordinates are not presented in *Table 4*.

Table 4.

The solubility relationships of micronutrient triads in 10=34=0 ammonium polyphosphate solution (See *Fig. 4*)

Micronutrient triad	Type of solid	The co-ordinates of point *P* g metal/100 g APP		
		α	β	γ
B-Mo-Zn	4*a*	1.75	1.00	2.08
B-Mo-Cu	4*a*	1.75	1.00	1.30
Fe-Mo-Mn	4*a*	2.70	1.00	0.07
Fe-Mo-Cu	4*a*	2.70	1.00	1.30
Cu-Fe-Cu	4*e*	1.30	2.70	0.67
Mo-Fe-Co	4*b*	1.00	2.70	0.67
Cu-B-Co	4*e*+	1.30	1.75	0.67
Mo-B-Co	4*b*	1.00	1.75	1.00
Cu-B-Fe	4*b*	1.30	1.75	3.66
Mo-B-Fe	4*b*	1.00	1.75	3.66
Fe-B-Co	4*d*+	3.66	1.75	1.00
Fe-Mo-Zn	4*g*	—	—	—
Zn-Mo-Cu	4*g*	—	—	—
Zn-Mo-Co	4*g*	—	—	—
Mn-Fe-Cu	4*g*	—	—	—
Zn-B-Cu	4*g*	—	—	—
Cu-Mo-Mn	4*g*	—	—	—
Co-Mo-Mn	4*g*	—	—	—
Zn-Mo-Mn	4*g*	—	—	—
Mo-Cu-Co	4*b*++	1.00	1.30	0.45
Mn-Fe-Co	4*h*	—	—	—
Mn-B-Zn	4*j*	—	—	—
Mn-B-Cu	4*j*	—	—	—
Zn-B-Co	4*h*	—	—	—
Mn-B-Co	4*i*	—	—	—
Mo-B-Mn	4*c*++	1.00	1.75	0.07
Mn-B-Fe	4*f*	0.03	1.75	3.66
Zn-B-Fe	4*h*	—	—	—
Cu-Fe-Zn	4*k*	—	—	—
Zn-Fe-Mn	4*k*	—	—	—
Cu-Mn-Zn	4*l*	—	—	—
Zn-Co-Mn	4*l*	—	—	—
Zn-Fe-Co	4*m*	—	—	—
Mn-Cu-Co	4*m*	—	—	—
Zn-Cu-Co	4*m*	—	—	—

Notes

+ The co-ordinates of point *P* cannot be given *from the solubility* data of micronutrient pairs.

++ Irregularities:

1. The solubility of Co is 0.45 g/100 g APP instead of the expected *0.67 g/100 g APP in the Mo-Cu-Co* system.
2. Based on the elaborated theory the Mo-B-Mn system could be represented by the solid *depicted* on *Fig. 4/1 c.* In practice *the* solid given in *Fig. 4/1 a.* represents the system, i.e. the solubility of manganese is 0.07 g/100 g APP instead of the expected 0.03 g/100 g APP value.

4. The Practical Application of the Method

In possession of the data presented in Chapter 3, it is feasible to meet the claims of rural economists and to decide whether is it possible to prepare the required solution of micronutrients from a 10-34-0 ammonium polyphosphate solution or not.

For systems containing two micronutrients the equations of lines bordering the plain figures can be set up using the symbols presented in *Fig. 3*. If the required concentrations of micronutrients are a_1 and b_1, the following conditions have to be fulfilled for the preparation of a precipitate free fertilizer solution:

In the case of 3.a:

The equations of the bordering straight lines are:

$$x=a \quad \text{and} \quad y=b.$$

The solution is stable, if $a_1 \leq a$ and $b_1 \leq b$.

In the case of 3.b:

The equation of the bordering straight line is:

$$\frac{x}{a}+\frac{y}{b}=1.$$

The solution is precipitate free, if:

$$\frac{a_1}{a}+\frac{b_1}{b}\leq 1.$$

In the case of 3.c:

The equations of bordering straight lines are:

$$x=a \quad \text{and} \quad y=\frac{c-b}{a}x+b.$$

The solution is precipitate free, if

$$a_1 \leq a \quad \text{and} \quad b_1 \leq \frac{c-b}{a}\cdot a_1+b.$$

In the case of 3.d:

The equations of the bordering straight lines are:

$$x=a \quad \text{and} \quad y=-\frac{b-c}{a}x+b.$$

The solution is precipitate free, if:

$$a_1 \leq a \quad \text{and} \quad b_1 \leq -\frac{b-c}{a}a_1+b.$$

For fertilizer solutions *containing three micronutrients* the construction of limiting conditions is similar, the difference is that in this case the equation systems are set up which describe the bordering planes of the spatial figure. The magnitude of the micronutrient concentrations a_1, b_1 and c_1 of the produced solution have to fulfil the demands prescribed by the equation system for the production of a precipitate free, micronutrient triad containing fertilizer solution.

The equation systems describing the solids depicted in *Fig. 4* (using the symbols of *Fig. 1* and *Fig. 4*) are as follows:

In case of 4.a:

$$\frac{x}{a} \leq 1; \quad \frac{y}{b} \leq 1; \quad \frac{z}{c} \leq 1.$$

It is to be seen that the solution will be precipitate free, if:

$$a_1 \leq a: \quad b_1 \leq b; \quad c_1 \leq c.$$

In the case of 4.b:

$$\frac{x}{a} \leq 1; \quad \frac{y}{b} \leq 1; \quad \frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

Clear solution can be produced, if:

$$a_1 \leq a; \quad b_1 \leq b; \quad c_1 \leq \frac{1}{c}-\frac{b_1}{cb}\left(1-\frac{d}{c}\right).$$

In the case of 4.c:

$$\frac{x}{a} \leq 1; \quad \frac{y}{b} \leq 1; \quad \frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

The conditions of the production of clear solution are:

$$a_1 \leq a; \quad b_1 \leq b; \quad c_1 \leq \frac{1}{c}-\frac{b_1}{cb}\left(1-\frac{d}{c}\right).$$

In the case of 4.d:

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{e}{a}\right) \leq 1; \quad \frac{y}{b} \leq 1;$$

$$\frac{x}{a}\left(1-\frac{f}{c}\right)+\frac{y}{b}\left(1-\frac{e}{a}-\frac{d}{c}+\frac{e}{a}\cdot\frac{f}{c}\right)+\frac{z}{c} \leq 1;$$

$$\frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

The condition of the preparation of the precipitate free solution is that the values of a_1, b_1 and c_1 have to be the roots of the above equation system.

In the case of 4.e:

$$\frac{x}{a} \leq 1; \quad \frac{y}{b} \leq 1;$$

$$\frac{x}{a}\left(1-\frac{e}{c}\right)+\frac{z}{c} \leq 1;$$

$$\frac{x}{a}\cdot\frac{d-e}{c}+\frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

The conditions regarding values a_1, b_1 and c_1 are the same as given in the case of 4.d.

In the case of 4.f:

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{e}{a}\right) \leq 1;$$

$$\frac{y}{b} \leq 1;$$

$$\frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

The conditions regarding values a_1, b_1 and c_1 are the same as given in the case of 4.d.

In the case of 4.g:

$$\frac{y}{b} \leq 1;$$

$$\frac{x}{a}+\frac{z}{c} \leq 1;$$

The solution is precipitate free, if:

$$b_1 \leq b \quad \text{and} \quad \frac{a_1}{a}+\frac{c_1}{c} \leq 1.$$

In the case of 4.h:

$$\frac{x}{a}+\frac{z}{d} \leq 1;$$

$$\frac{y}{b} \leq 1;$$

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

The conditions regarding values a_1, b_1 and c_1 are the same as given in case of 4.d.

In the case of 4.i:

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{e}{a}\right)+\frac{e}{a}\cdot\frac{z}{d} \leq 1;$$

$$\frac{y}{b} \leq 1;$$

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c} \leq 1.$$

The conditions regarding values a_1, b_1 and c_1 are the same as given in the case of 4.d.

In the case of 4.j:

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{e}{a}\right)+\frac{z}{c}\cdot\frac{e}{a} \leq 1;$$

$$\frac{y}{b} \leq 1;$$

$$\frac{x}{a}+\frac{z}{c} \leq 1$$

The conditions regarding values a_1, b_1 and c_1 are the same as given in the case of 4.d.

In the case of 4.k:

$$\frac{x}{a}+\frac{z}{c}\leq 1;$$

$$\frac{y}{b}+\frac{z}{c}\leq 1;$$

The solution is precipitate free, if:

$$\frac{a_1}{a}+\frac{c_1}{c}\leq 1 \quad \text{and} \quad \frac{b_1}{b}+\frac{c_1}{c}\leq 1.$$

In the case of 4.l:

$$\frac{x}{a}+\frac{y}{b}+\frac{z}{c}\leq 1;$$

The solution remains precipitate free, if:

$$\frac{a_1}{a}+\frac{b_1}{b}+\frac{c_1}{c}\leq 1$$

In the case of 4.m:

$$\frac{x}{a}+\frac{y}{b}\leq 1;$$

$$\frac{x}{a}+\frac{y}{b}\left(1-\frac{d}{c}\right)+\frac{z}{c}\leq 1.$$

The solution remains precipitate free, if:

$$\frac{a_1}{a}+\frac{b_1}{b}\leq 1;$$

$$\frac{a_1}{a}+\frac{b_1}{b}\left(1-\frac{d}{c}\right)+\frac{c_1}{c}\leq 1$$

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РЕЗЮМЕ

В ходе работы, направленной на определение растворимости в 10-34-0-ом растворе полифосфата аммиака семи наиболее важных микроэлементов — Ре(III), B, Zn, Cu, Mn, Co, Mo —, авторами был разработан такой метод, с помощью которого могут быть заданы соотношения концентраций металлов в растворе полифосфата аммиака, содержащего в себе три микроэлемента, при неизвестном составе и неизвестной константе устойчивости образующихся в растворе комплексов. Данный метод может быть математически распространён и на растворы удобрений, содержащие более трёх элементов.