

# MICRONUTRIENTS IN NITROGENOUS, PHOSPHATIC AND MIXED FERTILIZERS

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## INTRODUCTION

IN plant nutrition, besides carbon dioxide and water some other materials are also essential. Among them are: (a) The macronutrients nitrogen, phosphorus and potassium which are required by the plants in large quantity, (b) the secondary nutrients calcium, magnesium and sulphur which are required in lesser but still considerable quantity, (c) the micronutrients (trace elements) iron, manganese, copper, zinc, boron, molybdenum and chlorine, the requirements, of which are in extremely small quantity. The role of  $\text{CO}_2$ , water, macronutrients as well as secondary nutrients in plant growth are well known.<sup>1</sup> But, comparatively little information is available on the role of trace elements in plant nutrition. Presently, it is known that Fe is used by the plant in some of its respiratory enzyme systems like catalase and peroxidase. Besides, being essential in chlorophyll formation (though not a constituent of it), Fe deficiency causes leaves to turn white and results in retardation of growth. Zn is considered to be involved in certain enzyme systems in the plants like carbonic anhydrase and carboxylase. It is also associated with auxin, a growth-promoting hormone. Mn plays some unknown part in the functioning of certain oxidative enzyme systems as well as arginase and carboxylase groups. Cu is also probably associated with some of the plant enzyme systems such as polyphenol oxidase, laccase and ascorbic acid oxidase. In addition to the above-mentioned elements, it is possible that some more elements may be identified as essential elements and Rb is likely to be one among such elements.

The supply of macronutrients is the primary function of fertilizer industry. The requirement of secondary nutrients is usually met by incidental inclusion of these elements in major nutrient fertilizers. The occurrence of trace elements in fertilizers may be either accidental or due to their deliberate addition as micronutrients. As impurities in raw materials and during different stages of manufacturing processes, some of these elements find their way to the finished products.

The present work is based on the analysis of certain nitrogenous, phosphatic and mixed

fertilizers for K, Rb, Mg, Fe, Cu, Mn and Zn by Atomic Absorption Spectrophotometry.

## EXPERIMENTAL

The nitrogenous fertilizer (ammonium sulphate and urea) samples were brought into solution by dissolving in distilled deionised water. The phosphatic and mixed fertilizer samples were dissolved by two different digestion methods: (a) Digestion with conc. HCl and (b) digestion with  $\text{HF-HNO}_3$  (1 : 2). In each case a weighed quantity of the sample (~ 5 g.) was used and the solution made up to 100 ml. in a volumetric flask. Appropriate "blanks" were also prepared by adding only the respective reagents.

A Perkin-Elmer model 303 Atomic Absorption Spectrophotometer with Air-Acetylene flame was used for all the determinations. All the elements except K and Mg were determined directly in the sample solutions. K and Mg in phosphatic and mixed fertilizers were determined after suitable dilution (10 to 100 times) of the sample solutions. Usual precautionary steps were taken to avoid possible interference effects.<sup>2-4</sup> Considering the high solid contents in the sample solutions prepared, corrections were made in absorbance values for light scattering as suggested by Billings.<sup>5</sup>

## RESULTS AND DISCUSSION

The precision and accuracy of the determinations were checked by duplicate analysis and by adopting method of standard addition, and found to be within 2% and 5% respectively. Table I lists the sensitivity of determination

TABLE I  
Sensitivity\* and minimum sample concentration that could be estimated

Element	Sensitivity	Minimum determinable sample concentration ( $\mu\text{g/g}$ )
Calcium	0.45	0.9
Magnesium	0.02	0.04
Potassium	0.09	0.18
Rubidium	0.33	0.66
Iron	0.1	0.20
Copper	0.14	0.28
Zinc	0.175	0.35
Manganese	0.15	0.3

\*  $\mu\text{g/ml}$  of element which gives 1% absorption.

TABLE II (a)  
Concentration of various elements in nitrogenous fertilizers

Fertilizer	Sample treatment	$\mu\text{g/g. of the sample}$						
		Mg	K	Fe	Zn	Cu	Mn	Rb
Ammonium sulphate (F.A.C.T.) ..	Water dissolution	2	1	2.1	0.8	0.9	1.1	4.5
Ammonium sulphate (Gujarat fertilizers)	"	4	0.5	1.8	0.6	2	0.8	3.2
Urea (Gujarat fertilizers) ..	"	2	1.2	1.6	<0.35	2	0.6	4

TABLE II (b)  
Concentration of various elements in phosphatic and mixed fertilizers

Fertilizer	Sample treatment	% of the sample			$\mu\text{g/g. of the sample}$			
		Mg	K	Fe	Zn	Cu	Mn	Rb
Super phosphate (F.A.C.T.)	HCl digestion	0.1243	0.0155	0.1090	112	13	9	1.9
	HF-HNO <sub>3</sub> digestion	0.0400	..	0.0415	145	8	6	1.2
Diammonium phosphate (Gujarat fertilizers)	HCl digestion	0.2514	0.0402	..	402	14	99	1.2
	HF-HNO <sub>3</sub> digestion	0.0108	0.0343	0.2690	212	14	95	1.1
Factumfos (F.A.C.T.)	HCl digestion	0.1470	0.0098	0.0960	96	6	6.2	1.2
	HF-HNO <sub>3</sub> digestion	0.1030	0.0088	0.0990	106	6	7.9	1.1
Suphala (F.C.I. Trombay)	HCl digestion	0.3290	..	0.5125	38	10	57	30
	HF-HNO <sub>3</sub> digestion	0.1370	..	..	32	9	66	22.6

for different elements and minimum sample concentration in each case that could be estimated. Tables II (a) and II (b) report the concentration of various elements in nitrogenous, phosphatic and mixed fertilizer samples analysed. Of the two methods followed for phosphatic and mixed fertilizers, the values obtained by HCl digestion procedure are generally higher in case of K, Mg and Fe. For the rest of the elements, except Zn, the values obtained by both the methods agree well. No such generalization is possible in case of values for Zn from the results obtained. Hammar and Page who estimated micronutrients in fertilizers<sup>6</sup> favour HCl digestion method after trying KHSO<sub>4</sub> fusion, HF-HNO<sub>3</sub> digestion and HCl digestion methods. The data presented in Table II (a) show that the nitrogenous fertilizers analysed are deficient not only in micronutrients but also in K and Mg. Deficiencies of micronutrients are observed in the other two types of fertilizers also (Table II b).

Some of the typical guarantee values proposed and adopted by regulation in some states of U.S.A. are given in Table III. Unfortunately, the beneficial role of micronutrients added to fertilizers does not seem to be appreciated by the manufacturers in our country. It is desirable that quality control measures with

TABLE III

\*Typical guarantee values of certain micronutrients (Proposed and adopted by some states in U.S.A.)

Element	Per cent
Mg	0.50
Cu	0.05
Fe	0.10
Mn	0.05
Zn	0.05

\* Reported in Ref. (1).

regard to micronutrient content are strictly followed as is the case in U.S.A., where fertilizer manufacturers give guarantee values of these elements in their products.<sup>6</sup> It may be argued that the requirement of these elements by plants could be met with what is present in the soil and the range between adequate and toxic levels of micronutrients (like B, Zn and Cu) are small so that additional supply of the trace elements through fertilizers is not necessary. But, it is pointed out<sup>1</sup> that the dependence on incidental supply or, on materials already present in the soil, is not often adequate for optimum plant growth. Besides, the micronutrients which are already present in the soil are not readily available to the plant. Therefore, not only the supply of these nutrients, but also that in the available form (Cu, Zn,

Mn, etc., as sulphates and B as borate) is necessary. The view that micronutrients should be supplied as "insurance" whether a need can be identified or not is gaining support among agronomists.

Considering the problem of uniform distribution of micronutrients in fertilizers, analysis of random batch samples for their trace element content could be adopted as one of the quality control measures in fertilizer industry.

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## CRYSTAL STRUCTURES OF SOME ADDITION COMPOUNDS OF GLYCINE

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#### INTRODUCTION

IT is well known that glycine forms addition compounds with many inorganic salts. Even though the structure of glycine itself has been analysed in detail<sup>1-4</sup> very little structural information is available about these addition compounds. Hence, it was felt worthwhile to carry out a systematic study of the crystal structures of some of them to gather information regarding the orientation of the glycine units in its different compounds and also to elucidate the nature of the hydrogen bonds present.

This note describes the main features of the structure of glycine molecule in three addition compounds of glycine, viz., Diglycine barium chloride monohydrate, Diglycine strontium chloride trihydrate and Diglycine manganese chloride.

#### EXPERIMENTAL

The compounds were crystallised by slow evaporation of aqueous solution of glycine and the respective salt (barium chloride, strontium chloride and manganese chloride) in stoichiometric proportions. Morphological studies showed the crystals of barium and strontium compounds to belong to the orthorhombic system

while the manganese compound crystallised in the triclinic class.

Unit cell dimensions of the three crystals were determined from oscillation and Weissenberg photographs taken with  $\text{CuK}_\alpha$  radiation. The space groups were deduced from the symmetry of and the systematic absences in the respective X-ray diffraction patterns. The crystal data for all the three compounds are given in Table I. The present values for the

TABLE I

Crystal group	Barium compound Orthorhombic	Strontium compound Orthorhombic	Manganese compound Triclinic
Space group	$P_{bcu}$	$P_{bcu}$	$P\bar{1}$
Cell parameters	$a$ 8.302 Å	16.52 Å	4.971 Å
	$b$ 14.810 Å	9.34 Å	7.920 Å
	$c$ 9.324 Å	8.25 Å	6.976 Å
	$\alpha$ 90°	90°	107°·43
	$\beta$ 90°	90°	115°·96
	$\gamma$ 90°	90°	87°
Unit cell volume Å <sup>3</sup>	1143·0	1261·0	234·6
Density (measured) gm./c.c.	2·2	1·90	1·94
Density (calculated) gm./c.c.	2·182	1·892	1·932
Molecules per unit cell	4	4	1

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