

Minor Element Release from Organic-N Fertilizer Materials in Laboratory and Field Studies

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Activated sludge (AS), nitrogran tankage (NT), Peruvian guano (PG), and castor pomace (CP) were analyzed for Cu, Zn, and Mn. Acid leaching removed considerable quantities of these metals, part of which was in colloidal separates. Field studies on sandy soils, natively very low in minor elements, showed seasonal response by watermelons and cucumbers to fertilizer containing natural organic-N sources. A field experiment was conducted to determine the release of Cu and Zn into the soil using AS, PG, and CP in equal amounts to provide 1/3 of the N in a fertilizer. These organics also were tested either with or without added soluble minor elements, both before and after acid leaching. One treatment contained Everglades peat equal in weight to the organic matter in the organics used. Application of 1000 pounds per acre of fertilizer was made in two bands and repeated three times during the season. Soil samples from the fertilizer zone were analyzed by using water extraction followed by leachings with 0.1N HCl. Most of the N, K, and P from the fertilized zone was water soluble. Most of the Cu and Zn was released by the acid extraction where the organics or these minor elements were applied.

GOOD crop response to natural organic-N sources in fertilizer has been consistent in Florida, particularly between locations. Since many locations were previously unfertilized, minor elements supplied by the organics were suspected to be involved. However, the element or elements responsible for responses was unknown and unstudied.

Natural organic-N sources have been used in premium grades of fertilizer for many years. These materials have furnished the major source of water-insoluble N in these formulations, generally with the purpose of reducing leaching loss resulting from heavy rains in areas where high cost produce is grown. Since 10 to 50% of the N is commonly supplied by the organics in such fertilizers, the argument for slower N release must be recognized as only a partial explanation of favorable crop response, if any, from the organics. Other factors, such as serving as a source of minor elements, as microbial media, or as a buffer, and plant utilization of soluble organic compounds probably contributed to the responses obtained by growers (2, 9). The organics have continued to be used in many fertilizers because of their excellent conditioning properties (2). Supplies of most natural organics have fluctuated, the most constantly available being activated sludge produced by several

cities, castor pomace from Brazil, and Peruvian guano. Because labor costs are higher than fertilizer costs in growing many highly valued crops in Florida, most growers have used the more expensive fertilizers containing some organic-N and minor elements. All mineral fertilizers, in Florida, are generally used on field crops, pastures, and some vegetables and citrus.

The purpose of the present studies was to study responses found during some years for organic-N sources applied for watermelon and cucumbers, and to develop a technique for the measurement of the release of minor elements from organic-N sources in the fertilized soil.

Methods

Total analyses for plant tissue or organic sources were made on 2 or 5 grams of sample ashed in porcelain at 500° C. for 4 hours, and the ash was dissolved in 0.1N HCl. When boron was to be determined, 0.36N H₂SO₄ was used to dissolve the ash. Zinc was analyzed by the dithizone and thio-sulfate procedure (10). Copper was determined by the 2,2'-biquinoline method (1), Mn by the periodate method (10), Al by the modified aluminon procedure (11), and Fe as the orthophenanthroline complex (10). Flame photometry was employed using H₂-O₂ flame

at 554 m μ for Ca and 768 m μ for K analysis. Phosphorus was determined by the aminonaphtholsulfonic acid method (5). Organic-N was analyzed using the A.O.A.C. Kjeldahl method (7), ammoniacal and nitrate nitrogen by the Devarda method (7), and ammoniacal nitrogen by a Nessler technique (5). Boron was analyzed by using quinalizarin (5).

Water extraction of soil samples was made using 100 ml. of water per 50 grams of soil. The solution was shaken for 30 minutes and filtered through Whatman No. 42 filter paper. The soil and extraction flasks were washed four times with 25 ml. of water. Aliquots were taken for N, Ca, K, P, and Cu analyses. The filter paper and soil were returned to the extraction flask, and 100 ml. of 0.1N HCl were added. After being shaken for 30 minutes, the sample was filtered again and washed four times with 25 ml. of the acid. Aliquots were taken for NH₄-N, Ca, K, P, Cu, and Zn analyses.

Experimental

The formulations of fertilizers used in the experiment are shown in Table I. The fertilizer ingredients were all of commercial grade. The fertilizer with additional minor element mixtures analyzed 0.19% Mn, 0.05% Cu, 0.06%

Table I. Formulation of 4-3.5-6.6 (4-8-8) Fertilizer Used in Evaluating Minor Element Release

Material	Weight %		
	All mineral	1/3 Org. N	1/3 Org. N (leached)
Ammonium nitrate	6.00	6.00	6.00
Ammonium sulfate ^a	10.00	4.00	5.49
Superphosphate (20%)	40.00	38.65	38.65
Ammonium phosphate ^a			0.90
Sulfate of potash	16.00	16.00	16.00
Activated sludge		8.33	8.30
Peruvian guano		2.70	1.73
Castor pomace		7.82	8.33
Dolomite	12.80	12.80	12.80
Sand filler	13.50	2.10	0.17
Everglades peat ^b	8.57		
Soluble minor mix ^c	1.60	1.60	1.60

^a Replaces loss incurred by acid leaching of organics.

^b Used with all mineral fertilizer supplying 0.80% organic-N and used with 5.92 pounds of ammonium sulfate and 5.25 pounds of sand filler.

^c 1.60 pounds of Es-Min-El (Tennessee Corp.) in treatments 2, 4, 6, and 7 specified in Tables IV, VI, VII, and IX, and difference in sand filler made accordingly.

Table III. Yield of Charleston Gray Watermelons as Affected by Minor Elements and Organic Nitrogen at Gainesville, Fla.

Fertilizer Formulation	Yields, Tons per Acre			
	1958	1959	1961	1962
All mineral	10.9	6.4	3.8	12.2
All mineral with minor elements ^a			5.0	12.5
25% Natural organics	11.5	7.7	4.6	11.5
F value, 5%

^a Supplied by 15 pounds per acre of Ferro 501 frit; fertilizer grade is 6-3.5-6.6 (6-8-8).

^b Not significant.

^c Yield from all mineral fertilizer significantly less at the 5% level than yields from the other two treatments.

Table IV. Effect of Organic-N Source and Minor Element Mixes on the Composition of Watermelon Tissue at Gainesville, 1962

Fertilizer Formulation ^a	Minor Element Composition, P.P.M.							
	Young Plants				Mature Leaves			
	B	Fe	Cu	Mn	B	Fe	Cu	Mn
Inorganic only	26a	185	5.4a	119b	20a	74	3.9a	80a
Same + Frit 501	40b	221	6.3b	138c	30c	71	4.6b	112b
Same + Es-Min-El	38b	185	6.8bc	147d	27b	82	4.3b	118b
25% N from organics	28a	230	7.2c	105a	20a	82	4.6b	93a
F value ^b	Sig.	N.S.	Sig.	Sig.	Sig.	N.S.	Sig.	Sig.

^a Applied at 1600 pounds per acre in a split application; Frit 501 was used at 15 pounds per acre and contained 12.3% Fe, 4.9% Mn, 2.0% Cu, 4.0% Zn, 2.0% B, and 0.13% Mo; Es-Min-El was used at 10 pounds per acre and contained 2.0% Fe, 11.8% Mn, 3.2% Cu, 3.6% Zn, and 0.4% B; the organic-N source was Milorganite. Fertilizer grade is 6-3.5-6.6 (6-8-8).

^b Within each column, any two means without the same letter are significantly different at the 5% level by the Duncan's Range Test.

Zn, 0.03% Fe, and 0.006% B. The Everglades peat (EP) was ground to pass a 20-mesh sieve and fumigated with methyl bromide. The activated sludge (AS) contained 4.75% N, of which 0.30% was water soluble, and 2.6% P (6.00% P₂O₅). The Peruvian guano (PG) contained 15.0% N, of which 3% was water-soluble organic-N, 4.4% P (10% P₂O₅), and 1.6% K (2.0% K₂O). The castor pomace (CP) analyzed 5.20% N, of which 0.34% was water-soluble organic-N. The leaching of the organic sources with 3N HCl removed 0.30% of the 1.33% supplied as organic-N in the fertilizer. This loss was principally

colloidal and was 50% of the N in PG. In formulating the fertilizer, this loss was replaced by ammonium sulfate.

The field plot treatments were arranged in a randomized block with four replications. Charleston Gray watermelons were spaced 3 feet between hills and 10 feet between rows. Fertilizer was applied at the rate of 1000 pounds per acre in two bands on either side of the plant on January 4, 1963. A second side-dressing at the same rate was made on February 16, and a third on March 18. Location of each band was marked for soil sampling. The first three or four true leaves of the plants were taken for

Table II. Effect of N Sources on the Yield of Watermelons and Cucumbers at the South Florida Field Laboratory

N Source	Watermelon Yields, ^a Tons per Acre		
	1958	1959	1960
Sodium nitrate	13.1	18.7	2.8
Ammonium nitrate	15.3	23.6	8.9
Ammonium sulfate	18.6	27.2	19.3
30% Organic-N		36.0	39.4
L.S.D., 5%	2.3	6.4	5.1

	Cucumber Yields, ^a Tons per Acre		
	1960	1961	1962
All mineral	1.9	24.2	21.0
30% Organic-N	25.4	30.7	25.8

^a Fertilizer grade was 4-3.5-6.6 (4-8-8); in all cases where organic-N sources were used, yields were significantly better than with inorganic sources only, and ammonium sulfate was superior to the nitrate sources.

analysis 41 days after the first fertilizer application. Severe damage by *Fusarium* wilt occurred later in the growth and prevented yields being taken on many plots. Experimental conditions in previous years where yield data were obtained have been described (3, 6, 8).

Soil samples were taken by a 1-inch tube inserted 6 inches into the soil where the fertilizer was banded. The last sampling for three bands was made from a 1 1/2-inch core to a depth of 6 inches.

Results and Discussion

Yield Responses. Watermelon yields obtained at the South Florida Field Laboratory are shown in Table II. The degree of response to fertilizer containing the organic-N varied with years and was highly significant over the same rate and grade of all mineral fertilizer. Nitrate sources were less effective than ammoniacal sources, showing that nitrification was not likely to be the factor involved. The seasonal response also was a location response since new land was used each year; leaching losses also varied with the season. Cucumber yields, also shown in Table II, gave a consistent response pattern similar to watermelons. Since new land was used each year, the low level of fertility and the acid nature of the soil may have emphasized the properties of the organic-N sources. In the virgin state, this soil, primarily Immokalee fine sand, which has good exchange properties, has become leached of nearly all nutrients. The microbial population was probably at a low level prior to planting, and near the fertilizer it probably became very active as both energy source and nutrients were supplied. On somewhat better soils, such as phosphatic sands near Gainesville

Table V. Leaf Composition of Young Watermelon Plants from the Organic-N and Minor Element Experiment on Immokalee Fine Sand

Fertilizer Formulation ^a	Plant Composition									
	P.P.M.						%			
	B	Cu	Zn	Mn	Fe	Al	Ca	Mg	K	P
(1) All mineral	24	2.8	141	173	200	70	1.43	1.18	4.0	1.03
(2) Same as (1) plus m.e.	42	4.4	144	151	192	68	1.05	1.15	3.9	1.07
(3) 1/3 Organic N	23	4.7	123	156	193	71	1.25	1.26	3.6	0.98
(4) Same as (3) plus m.e.	40	4.0	142	163	143	65	1.03	1.22	3.5	0.96
(5) 1/3 Organic N leached	22	3.9	125	114	174	77	1.37	1.21	3.4	0.98
(6) Same as (5) plus m.e.	46	6.5	137	179	161	71	1.67	1.23	4.0	1.07
(7) Everglades peat plus m.e.	41	5.3	141	161	187	67	1.97	0.99	3.6	0.93
F values	b	b								

^a Organic-N supplied in equal amounts by activated sludge, castor pomace and Peruvian guano; Everglades peat used at same weight as the organic matter in the above organics.

^b Significant at the 1% level; other elements were not significantly different. Boron was increased in the leaves only where the minor element mixture was added to the fertilizer. Copper content was increased to a similar degree by the minor element mixture in Treatments 2 or where organic-N sources were employed except that addition of the soluble minor elements to the leached organics or with Everglades peat was also more effective than in Treatments 2, 3, 4, and 5.

Table VI. Soil Analyses of the Fertilized Band from Four Treatments 41 Days after Application

Fertilizer Treatment ^a	pH	Soil Analysis, ^b P.P.M.				
		Water Extractable			Acid Extractable ^c	
		N	K	P	Cu	Zn
All mineral fertilizer	5.04	470	449	228	0.89	3.37
1/3 Organic N	5.03	444	495	250	1.30	4.42
1/3 Organic N, acid leached	4.98	500	486	169	1.68	4.65
Everglades peat with all mineral fertilizer plus minor elements	4.72	493	504	372	2.14	7.28

^a Grade is 4-3.5-6.6 (4-8-8) applied at 1000 pounds per acre in bands placed on either side of the planting row; the sterilized Everglades peat replaced equivalent weight of the organic N sources which were equal weights of Chicago sludge, castor pomace, and Peruvian guano. See Table VII for complete list of treatments.

^b Water extractable N and 0.1N HCl extracted values were corrected for soil dilution in sampling to a common conductivity reading of 325 mmhos by using 50 grams of soil per 100 ml. of water.

^c Differences between means of 0.25 p.p.m. are significant for Cu, and 0.35 p.p.m. for Zn.

Table VII. Analysis of Fertilized Soil Sampled Prior to the Third Application of the Fertilizers

Fertilizer Formulation	Fertilizer Band ^a	Extractant Sequence	Soil pH	P.P.M.					
				N	K	Ca	P	Cu	Zn
(1) All mineral	1st	Water	4.98	382	473	508	102	0.09	
		0.1N HCl		48	63	558	147	0.60	2.55
	2nd	Water	5.01	192	332	1150	92	0.04	
		0.1N HCl		75	51	990	159	0.42	1.74
(2) Same as (1) plus minor elements	1st	Water	4.85	329	464	370	152	0.15	
		0.1N HCl		39	98	446	129	0.87	9.24
	2nd	Water	4.98	149	307	1020	111	0.13	
		0.1N HCl		40	55	955	207	2.42	27.55
(3) Same as (1) except N is 1/3 from organics	1st	Water	4.90	229	414	285	173	0.07	
		0.1N HCl		35	84	485	190	0.88	4.68
	2nd	Water	5.04	312	397	717	160	0.12	
		0.1N HCl		55	121	875	136	1.53	8.86
(4) Same as (3) plus minor elements	1st	Water	4.97	302	567	590	226	0.24	
		0.1N HCl		44	116	635	218	2.56	21.36
	2nd	Water	5.15	161	248	840	114	0.23	
		0.1N HCl		70	75	1085	138	2.81	24.31
(5) Same as (3) except organics acid leached	1st	Water	4.93	287	448	310	180	0.22	
		0.1N HCl		47	109	700	212	1.10	3.82
	2nd	Water	5.18	233	442	735	120	0.19	
		0.1N HCl		55	79	820	162	1.43	5.07
(6) Same as (4) except organics acid leached	1st	Water	4.87	319	489	895	171	0.55	
		0.1N HCl		87	146	513	225	2.20	26.05
	2nd	Water	5.34	242	388	407	108	0.40	
		0.1N HCl		70	75	1085	138	2.81	24.31
(7) Same as (2) with peat instead of organics	1st	Water	4.78	180	414	550	165	0.08	
		0.1N HCl		38	71	530	141	2.07	14.70
	2nd	Water	5.08	123	357	745	91	0.04	
		0.1N HCl		65	65	840	119	2.26	12.00
No fertilizer	Water	5.22	18	4	3	2	0.001		
	0.1N HCl		16	11	192	8	0.38	0.99	

^a First fertilizer band sampled 63 days after application and at same time second band was sampled 30 days after application. Copper values from the two bands were not significantly different but Treatments 2 through 7 gave significantly higher extractable Cu than Treatment 1, and Treatments 4 and 6 were higher also than Treatments 2, 3, and 5. Extractable Zn was significantly lowest in Treatment 1 and higher in Treatments 2, 4, and 6 than in Treatments 3, 5, and 7.

(6), watermelon yields have shown less response to organic-N sources (Table III). In experiments where responses to minor elements occurred, there was also a response to organics. This work did not, however, indicate which minor element was giving the response.

Tissue Analysis. Earlier spectrographic analysis of cucumber leaves indicated copper levels were higher where natural organics were used in the fertilizer. Tissue analysis of young plants and mature leaves (Table IV) indicated that Cu and possibly Fe and Mn were supplied to a similar extent by minor element mixes as by Milorganite. The young watermelon plants in the present study also showed higher Cu levels where the organics were used than where all mineral fertilizer was used (Table V). The soluble minor elements added also increased the B and Cu levels. The content of the other elements in the

leaves did not vary appreciably among the seven treatments. Zineb usually sprayed to control anthracnose was not applied prior to obtaining the leaf samples so that the Zn content was derived from only the soil and fertilizer.

Soil Analysis. The soil samples taken prior to the second side-dressing with the fertilizers showed both Cu and Zn extractable in 0.1N HCl were higher where organics were used than all mineral fertilizer (Table VI). The ratio of water-extractable N, P, and K was close to that in the fertilizer, indicating negligible loss or differential plant uptake up to that time. Soil samples taken prior to the third fertilization were analyzed in more detail (Table VII). The water-extractable plant nutrients were as high, or higher, from the first band as from the second. This probably resulted from lack of leaching and slow development of the watermelon

vines. Ditch irrigation of the beds also favored upward movement of the fertilizer. The water-extractable Cu was found by dialysis to be held by soluble organic matter and was very much less than the acid-extractable values. The acid-extractable N, K, and Ca probably were exchangeable, although carbonates and phosphates no doubt contributed to the Ca values accounting for the erratic variations. Both extractants removed similar amounts of P. The Cu values were significantly greater where the organics or minor elements were applied. This indicated that the values by acid extraction might be useful in studying the extent of Cu release by the organics as has been proposed for soils (4). The Zn values by this method also were higher where organics or minor elements were included in the fertilizer. Since Zn applied in the fertilizer was 1.2 times that of the Cu and the extracted Zn was from five to 10 times the extracted Cu, the authors assumed that Cu fixation occurred to a much greater extent than that for Zn. The acid treatment of the organics only slightly lowered the Cu and Zn that was extracted from the soil by the dilute acid. Table VIII shows that a considerable amount of Cu, Zn, and Mn was removed by the acid treatment of the AS, CP, and PG.

Soil samples taken 39 days after the third side-dressing were analyzed similarly to the previous samples, and the data are given in Table IX. The values for the respective elements from the three different bands were alike. Be-

Table VIII. Content of Cu, Zn, and Mn in Some Natural Organic Materials

Material	Treatment ^a	Composition			
		Ash, %	Cu, p.p.m.	Zn, p.p.m.	Mn, p.p.m.
Chicago sludge	None	25	580	276	1,550
	Acid leached	22	370	225	1,370
Castor pomace	None	7	40	325	220
	Acid leached	6	36	250	54
Peruvian guano	None	30	105	635	150
	Acid leached	8	55	325	31
Nitrogranitic tankage	None	20	135	460	225
Tung meal	None	1	30	75	200
Everglades peat	None	10	100	95	210

^a Material was thoroughly mixed before sampling and dry-ashed for analysis. The acid leaching was done with 3N HCl using equal volumes of acid and material in 4 cycles.

Table IX. Analysis of Fertilized Soil Sampled 39 Days after Application of the Third Sidedressing

Fertilizer Formulation	Fertilizer Band ^a	Soil pH	P.P.M. Extracted by 0.1N HCl							
			N	K	Ca	P	Cu ^b	Zn ^b	Cu ^a	Zn ^c
(1) All mineral	1st	4.87	657	808	832	367	0.24	3.6	0.18	3.9
	2nd	4.79	349	499	1,240	149	0.14	1.4	0.12	2.6
	3rd	4.86	361	522	1,300	210	0.17	2.0	0.15	2.0
(2) Same as (1) plus minor elements	1st	4.91	525	890	835	350	1.26	18.3	2.38	25.2
	2nd	4.62	399	441	791	138	0.88	9.2	1.45	20.8
	3rd	4.72	385	548	1,280	267	1.21	9.4	1.38	21.4
(3) Same as (1) except N is 1/3 from organics	1st	4.63	422	794	736	378	0.52	6.7	0.42	5.0
	2nd	4.55	439	545	1,460	352	0.99	20.3	1.19	18.1
	3rd	4.85	253	551	970	388	0.68	5.1	0.74	14.0
(4) Same as (3) plus minor elements	1st	4.69	424	627	833	471	1.80	9.6	1.75	21.2
	2nd	4.89	296	502	1,770	198	1.20	7.8	1.87	10.2
	3rd	4.87	340	549	1,810	454	2.88	24.4	2.68	24.5
(5) Same as (3) except organics acid leached	1st	4.80	394	738	897	465	0.84	5.9	0.86	8.9
	2nd	4.49	405	444	687	214	0.47	2.0	0.82	9.3
	3rd	4.81	554	527	730	296	0.38	6.0	0.91	14.2
(6) Same as (5) plus minor elements	1st	4.62	441	661	1,010	562	1.35	17.3	1.11	16.5
	2nd	4.92	390	484	525	232	0.67	15.2	1.65	16.4
	3rd	5.15	371	422	1,520	240	0.98	8.2	0.86	11.6
(7) Same as (4) with peat instead of organics	1st	4.65	452	940	561	291	1.64	11.9	2.56	30.0
	2nd	4.77	367	655	610	225	1.88	15.3	5.91	34.8
	3rd	4.87	441	562	1,110	296	1.33	11.7	1.83	17.0

^a Soil sampled at this time was 102, 69, and 39 days after application of the 1st, 2nd, and 3rd bands, respectively.

^b Adjusted to constant conductivity measured in water. Treatments 2, 3, 4, and 7 have significantly higher Cu and Zn extracted than treatment 5, the latter being also higher than Treatment 1. Bands not significantly different in amounts of these metals extracted.

^c Adjusted to constant acid-extractable P value of 243 p.p.m. Treatment 7 higher in Cu and Zn released than from the other treatments; Treatments 2, 4, and 6 similarly higher in both metals than Treatments 3 and 5; and Treatment 1 has, very significantly, the lowest values. Bands were not significantly different.

cause formation and settling of the bed was not uniform, difficulty was encountered in having the same proportion of soil and fertilizer drawn in each core. This was indicated both by the P values and conductivity. These values were adjusted to the maximum conductivity found and this value was assumed to represent the best sample of the band. Since the Cu and Zn were less likely to diffuse from the band than the more mobile major cations, this correction applied to these elements was imperfect. By using the acid-extractable P which represented less mobility, the values for Cu and Zn were corrected to a constant P value and are also shown in Table IX. These values showed less fluctuations and indicated similar trends for release from the soil where organics and minor elements were applied as found using the conductivity correction. Obviously the organic-N increased the extractable Cu and Zn, but it was rather surprising to find all three bands alike in the degree of the release, since microbial activity was involved in the breakdown of the organics. These values for Cu and Zn were so much higher than in the unfertilized soil that it can be concluded without much doubt that the organics provided more available Cu and Zn for the crop.

The Cu and Zn released by the acid extraction of the soil were probably from chelated forms originating from residual organic-N material and reaction with such groupings in the soil organic matter. Reactions with clay colloids were considered negligible since less than 1%

clay was present. Acidity has previously been found to release Cu from soils in which much of the Cu was suspected of being in the chelated form (7, 4). These soil extracts, at pH 1.2 to 1.8, contained cupric ions, since dialysis removed the copper from solution and since this copper did not react with biquinoline, which is specific for cuprous ion, until reduction with hydroxylamine took place. As shown in Tables VII, VIII, and IX, where the organic-N sources had been treated with 3*N* HCl, part of the Cu and Zn was removed. However, the high buffer capacity of these organics prevented the acidity of leachates from falling below pH 4.5 in contrast to the soil extracts above. The colloidal leachates from AS, CP, and PG were dark in color, and direct extraction of these with biquinoline or dithizone reagents removed a very small proportion of the Cu and Zn in the leachates. This suggested that these metals were bonded more strongly to the organic matter present than in the reagent complexes with these metals. It was further confirmed that the metals were held in the organic matter, since neither Cu nor Zn was removed by dialysis. In the soil, the stability of Cu and Zn organic complexes from the organic-N sources has not been studied. For several years, the authors have attempted to study substitution of inorganic and chelated sources of Cu, Fe, and Mn or minor element mixtures for minor elements probably released from organic-N sources. The present studies have narrowed the problem concerning

which elements and what rates should be used, and indicated that sampling in the band and acid extraction of the soil samples should assist in obtaining correlation data in future experiments.

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SOIL BORON DETERMINATION

Modifications in the Curcumin Procedure for the Determination of Boron in Soil Extracts

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THE most widely used method for determining microquantities of B in water extracts of soils is the curcumin procedure described by Dible *et al.* (2). While running many samples by this procedure, the author made several modifications in the method, thus allowing for greater reproducibility and accuracy.

Apparatus

Polypropylene beakers and centrifuge tubes.

Corning 728 glass reflux condensers and 100-ml. wide-mouthed extraction flasks.

Reagents

All reagents and standards are stored in polyethylene containers.

Flocculating Solution. Add slowly 1 gram each of Aerofloc No. 3171 and Superfloc No. 16 to ca. 400 ml. of hot, B-free H₂O, while agitating with mechanical stirrer. Continue heating and stirring until completely dissolved. Transfer to a 1-liter volumetric flask, cool, and bring to volume with H₂O. Both polyacrylamide polymers are presently known to be stocked by Fisher Scientific Co.

Extracting Solution. Dissolve 1 gram of reagent-grade CaCl₂·2H₂O in B-free H₂O in a 1-liter volumetric flask. Add

5 ml. of the flocculating solution and bring to volume.

Curcumin-Oxalic Acid Solution. To 400 mg. of curcumin and 50.0 grams of oxalic acid in a 1-liter volumetric flask add ca. 600 ml. of 95% ethanol. Heat gently with swirling until all reagents are dissolved. Cool, bring to volume with ethanol, and store in refrigerator.

Boron Standard. Dissolve 142.9 mg. of recrystallized H₃BO₃ in a liter of B-free H₂O. B concentration is 25 μg. per ml.

Dilute Boron Standard. Dilute 100 ml. of boron standard to 1 liter. B concentration is 2.5 μg. per ml.

Silicon Compensating Solution. Dissolve 1.265 grams NaSiO₃·9H₂O in a