

MULTI— ELEMENT DETERMINATION OF SOIL SOLUTION BY INAA

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(Received January 1991)

ABSTRACT

One factor of influencing crop growth is the effective elemental contents, especially trace elements, under the circumstances of the same concentrations of N, P and K in soil. In order to obtain the data of effective elemental contents in soil, a novel method was introduced. In this method, soil solution was extracted by a squeezer. The concentrations of elements in soil solution were determined by INAA. Study on the compositions and the contents of elements in soil solution will provide information on making a suitable soil environment for plant growth and for rational and economical manure.

Keywords: Soil solution INAA Trace elements

1 INTRODUCTION

At present, much attention is paid to study on the applications of trace elements in agriculture at home and abroad. Many books and articles relating to the application of trace elements in agriculture have been published. The studies started from the issues of the physiological disease caused by the deficiency of trace elements. Now the applications of microelements are being extended to raise the yield and improve the quality of crops.^[1-4] The effectiveness of applying trace elements is closely related to the effective trace element contents in soil. Thus, it is very important to determine these contents in plough horizon soil. Trace element data may provide the scientific basis for rational and economical manure. For example, the effective boron content in carbonate meadow soil, salinized meadow soil, sand soil, *etc.*, in Heilongjiang Province was less than 0.37 ppm, below the national standard of the effective boron limit value 0.50 ppm. Then, applying the boron fertilizer can increase the yields of crops very obviously.

Previous studies on effective microelements in soil were based on soil samples extracted with chemical agents in various media, such as oxalic-ammonium oxalate,

0.1 mol/l HCl aqueous solution, *etc.* However, there are some defects when extraction method is used. The procedure is laborious, and only one or a few elements can be analyzed by one kind of extraction medium.

In this study, a novel method was introduced. The information about the effective elemental content in soil was obtained by analyzing the elemental contents in soil solution, from which the roots of plants growing in soil can directly absorb nutrition and trace elements in mineral, clay mineral and humus^[5]. In this method, soil solution is extracted from soil by a squeezer. The contents of multielements in the soil solution were analyzed by INAA. The present method is simple, fast and able to determine many elements in one experiment.

2 EXPERIMENTAL

2.1 Preparation of standards and samples

Thirteen soil samples were collected from the wheat fields of the Dadun Agroecosystem Experimental Station, Beijing, at different sites and different growth stages of plant. The soil samples were dried at room temperature. Each sample was pressed to get original soil solution, about 30–40 ml, by a squeezer under the pressure of 9.8 MPa. A minute description about the squeezer will be given in another paper.

The soil solutions, 10–20 ml each, were preconcentrated in a quartz beaker by evaporation at low temperature of 60–70°C in a dustproof hood. The residues were transferred to a clean polyethylene film, further dried under an infrared lamp, and wrapped up with one sheet of Xinhua special filter paper and two layers of aluminum foil. The standards of multielement were prepared as follows: 50 μ l superpure standard solution with a known elemental content was pipetted on the six layers of filter paper with 9 mm diameter. The filter paper was dried in a drier, then wrapped with aluminum foil.

2.2 Analysis

The standards and the above-mentioned samples were irradiated in a nuclear reactor of the Institute of Atomic Energy for 7.5 h at a neutron flux of 5.4×10^{13} n/(s \cdot cm²). The irradiated samples were measured by a coaxial Ge(Li) detector system with IBM computer program control after cooling for 6 d and 15 d.

3 RESULTS AND DISCUSSION

The determination results of the contents of various elements in the soil solutions are listed in Table 1 and 2, where the soil samples 1–5 were taken from the same profile; samples 6–8 were collected in the same place but in different time of the day: morning, noon and evening, respectively; samples 9–11 were from productive, general and unproductive fields, respectively; samples 12–13 were taken at the stages of

seeding and heading, respectively.

3.1 Physiological function of microelements

The chemical compositions in the soil solution are very complex and vary from sample to sample, but all solutions contain more or less microelements. Some of them are essential for growth of plants, such as Zn, Se, Fe, Mo, Co, *etc.*; some harmful to growth, such as As, but the physiological function of other elements, such as Au, Sc, rare earth, are unclear. Most elements, except Ca, Zn, As and La, in the soil solutions are within the ranges of their background levels in natural water. The concentrations of Ca and Zn in the soil solution are larger than those in natural water, which is probably due to the parent rock of soil or the decomposed products of organic fertilizer. The excess As probably comes from the pesticide residues.

Table 1
The contents of elements in soil solutions of 1 m soil profile

ng/ml

Element	Sample 1 (0—20 cm)	Sample 2 (20—40 cm)	Sample 3 (40—60 cm)	Sample 4 (60—80 cm)	Sample 5 (80—100 cm)
Sm	0.27	0.05	0.09	0.05	0.09
Ca	225000	175000	173000	155000	121000
Sb	1.70	0.56	1.00	0.46	0.45
Br	32.5	90.4	151.0	122.0	108.0
Na	55600	45400	49700	37900	34700
La	0.61	0.48	0.44	<0.21	<0.21
U	3.18	<0.54	0.74	<0.54	1.37
Yb	<0.14	<0.14	<0.14	<0.14	<0.14
Ce	1.28	0.81	0.95	1.20	0.93
Se	<1.80	1.84	2.01	1.90	<1.80
Th	<0.18	<0.18	<0.18	<0.18	<0.18
Cr	1.81	1.67	3.84	1.81	<0.92
Hf	<0.11	<0.11	<0.11	<0.11	<0.11
Sr	2760	1720	1040	600	990
Nd	<7.6	<7.6	<7.6	<7.6	<7.6
Cs	<0.11	<0.11	<0.11	<0.11	<0.11
Tb	<0.095	<0.095	<0.095	<0.095	<0.095
Sc	0.046	0.032	0.052	0.082	0.031
Fe	155	101	217	378	101
Mo	7.06	5.72	4.83	3.03	4.33
Au	0.015	0.005	0.014	0.008	0.009
As	1.95	3.91	2.57	<0.9	2.92
Zn	447	<24	1460	2260	254
Ta	<0.28	<0.28	<0.28	<0.28	<0.28
Co	7.15	2.99	9.80	8.39	1.57
Eu	<0.15	<0.15	<0.15	<0.15	<0.15
Lu	<0.07	<0.07	<0.07	<0.07	<0.07
Ba	174	137	356	211	185
Rb	8.8	<6.2	11.9	10.6	<6.2

3.2 Contents of elements in different soil profiles

Concentrations of elements in soil solutions vary with different depths of soil profile in a range of 1 m. There are three cases: (a) Some elements, *e.g.* Sm, La, U, Ce, Sr, Mo, Au, Ca, *etc.* are relatively rich in the soil solution from the top soil layers. (b) Yb, Th, Hf, Nd, Cs, Tb, Sc, Ta, Eu, *etc.* do not significantly change in the profile. (c) The contents of Br, Fe and Zn in the surface layer are less than those in the bottom layers.

Table 2
The contents of elements in soil solutions of different soils

ng/ml

Element	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	In nature water
Sm	0.80	0.62	0.52	0.43	0.48	0.16	0.32	0.50	
Ca	250000	265000	233000	599000	420000	398000	290000	531000	10000—100000
Sb	1.41	1.64	1.41	1.81	1.63	1.17	0.93	1.27	0.1—1.0
Br	49.1	41.6	48.5	46.5	57.3	68.4	64.6	50.0	
Na	48300	48700	43900	53100	66800	43700	46200	39600	1000—100000
La	0.56	0.40	0.36	0.67	0.60	0.66	<0.21	0.5	0.01—0.1
U	11.2	8.02	6.74	6.22	6.34	1.90	4.33	6.96	0.01—10
Yb	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	<0.14	
Ce	3.83	3.33	2.66	3.14	3.14	1.10	1.81	3.16	
Se	1.80	2.51	2.67	<1.80	2.07	2.25	2.42	2.35	
Th	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	
Cr	1.86	1.31	1.85	1.04	<0.92	<0.92	<0.92	1.38	0.1—100
Hf	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	
Sr	3220	3180	2720	6840	5140	4510	3900	5120	
Nd	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	
Cs	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	
Tb	<0.095	<0.095	<0.095	<0.095	<0.095	<0.095	<0.095	<0.095	
Sc	0.026	0.033	0.031	0.056	0.044	0.031	0.050	0.029	0.001—0.10
Fe	147	106	111	181	136	150	109	133	10—1000
Mo	3.89	6.86	6.53	2.24	4.02	2.72	5.13	1.59	1—10
Au	0.014	0.015	0.010	0.019	0.010	0.013	0.005	0.005	0.001—0.1
As	3.52	3.04	2.83	3.54	6.82	1.92	4.49	1.87	0.01—1
Zn	598	674	517	1310	238	1560	<24	1250	1—100
Ta	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	<0.28	
Co	4.62	4.06	3.47	5.17	4.69	5.60	9.03	4.92	0.1—10
Eu	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	0.001—0.1
Lu	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	
Ba	202	196	225	365	181	128	130	205	
Rb	<6.2	<6.2	<6.2	<6.2	9.2	7.46	7.78	<6.2	

3.3 Concentrations of elements in soil solutions at different growth periods of wheat

The concentration changes of Co, Mo, As, Zn and Ca in soil solutions at different growth periods of wheat are clear. For example, the content of Mo is 5.13 $\mu\text{g/l}$ in the seeding stage, 1.59 $\mu\text{g/l}$ in the heading stage and blooming stage, and 7.06 $\mu\text{g/l}$ in the mature stage.

3.4 The variation of the element contents in a day

Although samples were taken on the same day (1988—06—08), the concentrations of some elements in soil solution changed from time to time. For example, the contents of Ca, Zn, and Sb in the soil sample taken at noon were greater than those in the samples taken in the morning and the evening, which is probably related to increased solubility caused by the higher temperature at noon. The temperature of soil in 0—25 cm plough horizon was 13.5°C at morning, 19°C at noon and 16°C at evening, respectively.

As Br is more volatile, its content in the soil at noon, and in surface layer was less than that in the morning or evening, and in the deeper layer. But, the contents of Sm, La, U, *etc.* in the soil in the morning were the largest in that day. The cause is still unknown.

3.5 The contents of the elements in the soil solution of different wheat field

There were more Ca, Fe, Cr, Sr, Sc and Ba in the soil solution where the wheat grew better (it refers to that: the stems of the wheat are higher and the colour of the leaves look normal). Among them, Ca, Fe, Cr and Sr had obvious effect on promoting the crop growth. For an instance, in the counties around Jinhua City, Fujian Province, most of the soil was acidic or weakly acidic, the yields of the wheat and barley were low and unstable for many years. Since lime was applied as a fertilizer, the yield of the wheat has increased by about 11%^[6]. Obviously, the cause is the increase of the Ca ion in the soil. As calcium ion can eliminate the poisonous effect of other cations, such as Mn, Al, *etc.* and promote the metabolism of carbon and nitrogen in the wheat stems. The importance of iron in plants lies in two aspects: on the one hand, iron is closely related to the oxidation and reduction processes in body of plants; on the other hand, iron is an essential factor for formation of chlorophyll of plants.

3.6 The comparison between the present method and the extraction method

Liu Zheng *et al.*^[7] extracted the effective elements, B, Mo, Zn, Cu, Mn, *etc.* from the soil using several extractants. For example, Mo was extracted by GRIGG's solution, Zn and Cu in an acidic soil and a calcareous soil were extracted by 0.1 mol/l HCl aqueous solution and by a DTPA solution at pH 7.3, respectively. In the extraction method, only one or a few elements are analyzed by one extractant.

In this work, the combination of the pressing method for preparing the soil solution and NAA determination makes it possible to analyze tens elements in one experiment. If a combination of long and short irradiations is adopted, more information about the elements in the soil solution can be obtained.

The effective Zn content in calcareous soil of North China reported by Liu Zheng *et al* was from trace to 3 ppm with an average values of 0.37 ppm, while most values were less than the critical value (0.5 ppm) of Zn. In this work, the concentration of Zn in the soil solution obtained by squeezing the soil was from trace to 1.6 ppm and most

values were about 0.5 ppm.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. Chai Chifang and Dr. Chen Tongbing for their help.

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