EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF COBALT IN SOILS BY THE APPLICATION OF IODINE NITROTETRAZOLE CHLORIDE (INT)

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ABSTRACT
An extraction-spectrophotometric method for cobalt determination in soils by the application of iodine nitrotetrazole chloride (INT) was developed and compared to atomic absorption spectrometry (AAS). The method investigated characterized with expressivity, selectivity and satisfactory accuracy.

Keywords: Co, INT, soils, AAS, spectrophotometer, methods.

INTRODUCTION
The application of trace elements as fertilizers turned out as one of the basic conditions for yield increase of the agricultural crops and for the improvement of their quality. The latter statement is proved by the fact that the extraction of trace elements is increased and their content in soils decreases with the yield increase. Moreover, due to the influence of the increased doses of micro fertilizers the mobility of some trace elements is reduced as a result of the formation of their hardly accessible forms. Thus, further investigations on the content of some trace elements such as the cobalt, is required.

In the literature there is no sufficient data concerning the physiological function of cobalt in the plant organism, only some authors display that this trace element is essential for the nitrogen, phosphate and carbohydrate exchange (1). It was established that cobalt influences the physiological processes which determine plants drought and heat resistance. Probably, due to the effect of cobalt, the energetic exchange in plants is improved (2). Cobalt significantly increases the content of chlorophyll a and b. It, also, positively affects the synthesis and accumulation of soluble sugars and starch in some plants. One of the most important functions of cobalt is its participation in the synthesis of vitamin B\textsubscript{12} compounds, as well as its influence on the exchange and formation of vitamins E and A, carotene, ascorbic acid, and etc.

Cobalt content in the surface soil layer is usually in the range 0.1 – 50 mg/kg. It was established that cobalt in soil is a constituent of the soil alumsilicates, is adsorbed on the surface of the mineral and organic colloids, and forms complex compounds with the organic substances. The determination of the assimilating forms of the trace elements is essential for the estimation of soil fertility and for the proper application of micro fertilizers.

As it is well-known, cobalt content in the agrochemical objects is insignificant. Thus, extraction-photometric methods are used for the determination of ultra small cobalt quantities in these objects. Photocolorimetry, polarography and spectroscopy are among the most widely applied techniques (3). Simplicity, quickness and accessibility are the basic advantages of the photocolorimetric methods. The reactions between cobalt (II) and nitroso-R salt (4), and between cobalt (II) and...
nitrosochromotropic acid in the presence of SCN\(^-\) (5) are widely used in the analytical practice. The main disadvantages of cobalt photometric determination in soil and plant samples which reduce the accuracy of its determination are the presence of colored organic substances and/or some ions like iron, nickel and copper. (6).

The goal of the present study is to elaborate an extraction-photometric method for cobalt determination with INT in soils, that surpasses some of the currently used methods in selectivity and expressivity, as well as to examine its applicability for various soil types.

**MATERIALS AND METHODS**

**Apparatus**

The spectrophotometric determinations were accomplished on Spekol, Carl Zeiss Jena, Germany, \(\lambda_{\text{max}}\) 630 nm. The atomic absorption measurements were performed on a double beam atomic absorption spectrophotometer PYE UNICAM SP 1950 equipped with air/acyetylene flame ZEEMAN PERKIN ELMER 3030 with a graphite furnace HGA 600 and pyrolitic graphite tubes as an atomizer (ETAAC).

**Reagents**

Double distilled water was used for all procedures. All reagents were p. a. (p.a. Merck and Fluka). The initial standard Co solutions with concentration 1000 mg/dm\(^3\) were supplied by Merck, Darmstadt Germany.

**Samples**

Three certified soil samples corresponding to two basic soil contents in Bulgaria: light alluvial-deluvial meadow soil PS-1, COOMET № 0001-1999 BG, SOD № 310a 98, light meadow cinnamonic soil PS-2, COOMET № 0002-1999 BG, SOD № 311a 98 and light alluvial-deluvial meadow soil PS-3, COOMET № 0003- 1999 BG, SOD № 312a 98, were used in the study. Cobalt content in four soil types, namely leached cinnamon, chernozem, opodzolen chernozem and alluvial, was analyzed. The samples were taken at 0 - 20 cm soil layer depth.

Sample preparation for AAS determinations was accomplished according to DIN ISO 11466, 1997 (7).

**Cobalt extraction**

5 cm\(^3\) soil samples, some drops of 1 M NaOH (for adjustment to pH 9.0-10.0) and 5 cm\(^3\) 0.02% dithizone in chloroform were consecutively placed in 100 cm\(^3\) separating funnels. The systems were left to extract for 1 min. Adequate quantity of HCl (1:1) (for adjustment of pH 1.0-2.0) and 2 cm\(^3\) 4 M thiocyanate solutions were added to the organic phase. Re-extraction for 1 min was accomplished. The organic phase was discharged, while 1 M NaOH (for pH 3.0-4.0), 0.6 cm\(^3\) 1.5x10\(^{-2}\) M INT and 2 cm\(^3\) saturated solution of ascorbic acid (for masking of the interfering ions) were added to the aqueous phase. Distilled water was supplemented to a volume of 20 cm\(^3\). Extraction with 3 cm\(^3\) 1,2-dichloroethane for 30 s was accomplished. After the stratification of both phases, the organic was filtered through a paper filter, placed in a cuvette, b 1 cm, and photometered at \(\lambda\) 630 nm. A blank, not containing a soil sample, was also analyzed for reliability of the experimental results.

**RESULTS AND DISCUSSION**

Fig. 1 displays the data for Co content in the three certified soil samples. The results obtained during the recent investigations ascertained that the extent of cobalt extraction related to the certified value according to both methods was good.

The results for Co content in the four basic soil types distributed in Bulgaria are presented on Fig. 2. According to the comparative estimation of the analytical methods applied for Co determination in soils, it was established that the spectrophotometric method measured higher Co concentrations in the leached cinnamon and alluvial soil samples than AAS, while the latter detected higher content of the trace element in the chernozem and opodzolen chernozem samples.

Krause R. (8) stated that soil characteristics influenced the extent of Co extraction from various soil types. It was supposed that in most of the cases Co binds to the soil minerals (iron and manganese oxides, carbonates and clay minerals) through isomorphous substitution and fixation in vacant structural positions (9). Besides the great number of scientific publications on the methods of sample preparation and the availability of national and international standards, the comparative investigations displayed significant divergences in the results obtained by different laboratories. Identical methods could not be applied with the same success for various soil types.
Fig. 1. Co content in the certified soil samples determined spectrophotometrically and by AAS related to the consensus value of the referent material.

Fig. 2. Co content in the four soil types determined spectrophotometrically and by AAS.

Cobalt is a trace element which, in small quantities, is necessary for plants, animals and man. In high concentrations, however, it is a hazardous pollutant that, by the biological cycle, passes along the food chain to man, thus causing a variety of diseases. According to some geobotanical investigations (10), increased heavy metal concentrations, including Co, in soil, caused pathological changes in plants provoking yields decrease and quality deterioration of plants production.

The cited in the present study newly developed extraction-spectrophotometric method with INT excelled in selectivity and expressivity some of the previously used techniques for cobalt determination in soils. It could, also, be applied for various soil types. Consequently, the method is quick, easily applicable and sufficiently accurate to satisfy the practical needs of agriculture and ecology.
CONCLUSIONS
The developed in the recent study extraction-spectrophotometric method for cobalt determination in soils with iodine nitrotetrazole chloride (INT) characterized with expressivity, selectivity and satisfactory accuracy. According to these indices, the method elaborated excels some of the currently applied techniques for Co determination in soils.

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