

BERYLLIUM IN ADOBE-DERIVED SOIL OF CAVITE

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ABSTRACT

This study ensued from the speculation that something in the soil of certain areas in Cavite was contributory to, if not the main cause of abnormalities in plants, especially during the driest part of the year (March to May). To identify it, extracts of the soil were fractionated. The fraction which was precipitated by ammonium hydroxide was tested for its constituent elements. Strong indications pointed to beryllium as the unusual element; this was confirmed by its production of the corn-flower blue reaction with quinalizarin. Quantitative separation with 8-quinolinol, and final precipitation as its hydroxide gave fairly high results for beryllium.

Introduction

Velasco (1985) presented a light-hearted account of the antecedents which led to his choice of the problem concerned with adobe-derived soil. This intriguing topic which involves the psychology of making a choice is tempting to elaborate on, but it may not be pertinent at this time.

It may suffice to state for the time-being that the paper left the writers with a feeling that there was still a blind spot in the knowledge about this kind of soil. While it may be true that boron deficiency caused in part the abnormal growth of some plant species in the locality, it was possible that another soil factor could be contributing to the abnormal condition; hence, this study. This project was conducted in the Plant Physiology Laboratory, Institute of Biological Sciences, UPLB, from January 1985 to June 1986.

Material and Methods

The soil

This is tentatively classified as Guadalupe clay. It is almost black and very sticky when wet; ash gray and blocky when dry. It forms an over-burden, about one foot thick, on a substratum of adobe rock.

The substratum

The adobe rock is apparently in various stages of sedimentary formation. At some places it is thick, compact and homogenous; at others, it is thin, and immediately underlain with sand and sandstone. At a depth of 60 feet, the material (brought up during well-drilling) consists of black, hard bits of rock or grains of sand.

Ground water

The water which comes out of the artesian well is clear and fresh. However, on being boiled, it leaves a thick incrustation on the walls of the vessel. When the water in the field evaporates in the sun, it leaves white, scaly flakes on the surface of the soil. Used for dissolving zinc sulphate, the water immediately turns turbid, followed by the formation of white flocculent precipitate.

Analytical methods

In fractionating the soil extract into various groups, the scheme of A.A. Noyes (cited by Weast, 1978) qualitative analysis was used. As exigencies demanded, slight modifications were adopted.

Details of the analytical procedures are presented in the experiments.

Experiments and Results

Attempts to identify the element

During the first few attempts to fractionate the extract into the various groups of elements, the leachate from about 20 kilograms of soil was used as starting material. The leachate was chosen because (a) the element was apparently water-soluble, and (b) very little iron was expected to be present in the leachate; hence, it would not present complications in the fractionation. The leachate was evaporated to about one-fiftieth (1/50) of its original volume. This concentrated extract, when acidified with hydrochloric acid, turned yellow with a tinge of green.

To bring down the acid-insoluble sulphides (Cu-As), sodium sulphide was used to replace hydrogen sulphide. The former was expected to form hydrogen sulphide on reacting with the hydrochloric acid in the extract. The curious observation was that everytime a dose of sodium sulphide was added, a flock of tiny white crystals was formed. These crystals disappeared on stirring, but persisted when the pH came up to about 6. Zinc was among the elements which formed insoluble white sulphides at almost neutral pH; hence, its presence was considered most likely. It was speculated that zinc could be in excess. However, the quantitative analysis for the element showed that, if at all, it was slightly deficient (Velasco, 1985).

With the repeated attempts at fractionating the extract, it became apparent that the element being sought belonged to the group of insoluble hydroxides. Freed

of iron, this group produced a white, flocculent precipitate with ammonium hydroxide. Part of the precipitate tended to stick to the walls of the beaker.

Because some of the reagents needed in the systematic separation within the group was not readily available, the writers assumed by turns the presence of each element, and proceeded with the confirmatory test. The following elements were shown to be absent: V, Ta, Nb, Cr, Ga, In, Ti, Zr, and Sn. Aluminum, although present, was not suspected of causing some trouble because the soil was almost neutral in reaction. The only other member of the group was beryllium but the writers did not have much hope of meeting it since it is rather rare. When they half-heartedly tested for the element, the extract surprisingly produced the prescribed cornflower blue color with quinalizarin. A blue precipitate was formed when the mixture was allowed to stand for some time, while the blank remained clear and maintained the violet color of quinalizarin. When the aluminum was separated from the beryllium fraction, the reaction of the latter with quinalizarin became more distinct.

The amount of beryllium recovered from the soil and the adobe rock

The writers set out to compare the amount of beryllium recovered from the soil by (a) extraction with dilute hydrochloric acid, (b) digestion with a mixture of concentrated sulphuric acid and nitric acid, and (c) fusion with sodium carbonate. However, they postponed this objective after a few attempts because they found that the separation of beryllium from aluminum was a critical step. To develop a workable technique of separating the two elements, they tried two methods.

C.L. Parsons (cited by Mellors, 1957) recommended that for this purpose, the neutral solution containing aluminum, iron and beryllium should be saturated with crystals of sodium bicarbonate. The liquid is warmed for 24 hours with frequent shaking. Most of the beryllium passes into the solution, while aluminum and iron are precipitated — completely, if other salts are not present. By blowing steam through the filtrate until it reaches its boiling point, the beryllium will be completely precipitated as granular basic carbonate.

In this project, this procedure did not yield consistent results.

The separation procedure recommended by E. Booth (cited by Wilson and Wilson, 1962) using 8-quinolinol (8-hydroxy quinoline) was also tried. The acid solution was carefully adjusted to pH 5.7 with dilute ammonia and hydrochloric acid; then it was treated (slowly with stirring) with 5 percent 8-quinolinol in 2N acetic acid, followed by ammonium acetate until a permanent precipitate was obtained, at which point 2-25 ml of the latter was added in excess. The mixture was digested at 60-75°C for 15 minutes; the precipitate was filtered off through a sintered glass bottomed (or asbestos-lined) Gooch crucible. The precipitate was washed 5-6 times with 0.1N ammonium acetate adjusted to pH 5.7. The beryllium was recovered from the filtrate and washing.

With the latter method, the data presented in Table 1 were obtained.

Table 1. Amount of beryllium oxide obtained from 10 grams of soil and of adobe rock

<i>Material</i>	<i>Replication</i>	<i>Grams BeO</i>	<i>Percent BeO</i>	<i>Percent Be</i>
Soil	1	0.3844		
	2	0.2919		
	3	0.5783		
	Ave.	0.4182	4.18	1.50
Adobe Rock	1	0.0601		
	2	0.2490		
	3	0.3840		
	Ave.	0.2310	2.31	0.92

Compared with the average concentration of beryllium in the earth's crust (3 to 6 ppm), the concentration in this sample (1.5 percent, or 15,000 ppm) seems to be considerable. Probably the beryllium isolate in this trial was not pure. It will be sent to a better-equipped laboratory for a more exact determination.¹

Assuming for the time being that there is a real difference (in the concentration of the element) between the soil and the adobe rock, this may be taken as an indication that a rich deposit may be found at the level of the water table or deeper. Perhaps the element accumulated in the soil as a result of repeated watering of plants, especially during the dry season, with ground water drawn from wells.

Discussions

The writers would like to point out some difficulties which were spawned by the country's stringent foreign exchange position and its negative effects on imports, resulting in paucity of laboratory supplies. Since reagents were not readily available, the writers considered three alternative approaches: (a) using substitutes for standard agents, (b) making the reagent in the laboratory, and (c) adopting instrumental methods of analysis.

a. The writers figured that hydrogen sulphide would be produced when sodium sulphide was added to the extract containing hydrochloric acid. However, they failed to consider that sodium sulphide could react directly with some component of the system even before hydrogen sulphide could be evolved. As a re-

¹ Postscript: An isolate from the soil was kindly analyzed by Professor Kiyotoshi Morishige, Department of Chemistry, Faculty of Science and Technology Kinki University, Osaka, Japan. It was found to contain 166 micro-gram of beryllium per 0.05 gram of sample. This comes out to be 3.32 mg/g, or 0.3 per cent (Personal communication, January 1987).

sult, they made an erroneous guess on the nature of the element sought. The white crystals which the writers observed were, according to the literature, beryllium hydroxide crystals and not the putative zinc sulphide. Apparently, sodium sulphide reacted with water to form sodium hydroxide, and the latter reacted with the beryllium ion.

b. The standard method of evolving hydrogen sulphide is to make ferric sulphide react with hydrochloric acid in a separate vessel. However, most of the local supply houses did not carry ferric sulphide in their stock. The single store which did was charging ₱350 per kilo.

An alternative method of evolving hydrogen sulphide was tried; that is, paraffin, sulphur and asbestos in a certain proportion were mixed and heated. The procedure was not satisfactory because the proportion changed as the reaction proceeded. Hence, the gas contained not only hydrogen sulphide, but also paraffin, sulphur, and other constituents.

The writers reverted to the standard procedure. They tried making the ferric sulphide from iron filing and sulphur. The process might not have been efficient, but a product was obtained anyway.

Needless to say, the exploration of these ways consumed a lot of time.

c. Those of us who have had training in modern techniques would probably be wondering whether or not the writers explored the use of modern equipment in the IRRI, NIST, UP, etc. They did consult with people in these agencies. However, most of their equipment were not operational for lack of a part, such as the right cathode tube, or for lack of reagent. Another impediment was the lack of time. The researchers consulted had their own pet projects and to them, time spent in accommodating the request was time withdrawn from their project.

Perhaps the local scientific community should pay more than passing attention to the beryllium deposit in our midst, because beryllium has many important uses in technology and in industry. The alloy is used in springs, electrical contacts, spot-welding electrodes, non-sparking tools, high speed aircraft, missiles and spacecraft. The metal is used as reflector and moderator in nuclear reactors due to its low absorption cross-section for thermal neutrons. When bombarded with alpha particles, it produces many neutrons. Due to its stiffness, lightness and dimensional stability, it is used in gyroscope, computer parts and inertial guidance instruments. It has a high melting point, high permeability to x-ray and is non-magnetic. These properties may be advantageous in as-yet uncharted uses.

As vacuum-cast billet, the metal cost \$70 per pound in 1977 (Handbook of Chemistry and Physics); as copper-beryllium master alloy, it cost \$265 per kilo. J.T. Baker quoted beryllium sulphate tetra hydrate at \$23.45 per 10 grams.

The high price of the metal is attributed not only to its great demand but also to its relative scarcity. The estimated concentration in the earth's crust ranges from 3 to 6 ppm; shales are reported to contain an average of 0.37 ppm, while coal ash has 4.0 ppm. The biggest source of commercial beryllium is beryl ($3 \text{ Be O} \cdot \text{Al}_2 \text{O}_3 \cdot \text{SiO}_2$) whose computed content of the element is 5 percent.

The standard extraction and separation procedures may not be economical because sulphuric acid and the other reagents are rather expensive. We should explore the less direct but more inexpensive procedure, although it is slow and time consuming. For example, irrigation water from artesian wells may be put in concrete tanks and treated with a little sodium sulphide to precipitate the beryllium, as compact crystals of its hydroxide; however, the residual sulphide might be objectionable. Alternatively, sodium hydroxide can be used. That the hydroxide formed with the latter reagent is flocculent may not be very objectionable, because a way of handling it properly could be devised.

From another standpoint, beryllium should be studied as a potential health hazard. There have been reports that workers in beryllium-using factories develop skin and respiratory diseases. There are as yet no clear indications that those who ingest beryllium through food and water suffer any trouble. If experiments would show that they do, then the people living in places with beryllium deposit should be forewarned.

Beryllium should also be studied as a problem in crop growing. A survey should be made to find what species are sensitive to it, and how its detrimental effects could be minimized, if not neutralized.

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