TRACE ELEMENTS AND AGRICULTURE

By C. L. GRANT

Engineering Experiment Station, University of New Hampshire
Durham, New Hampshire

In the last issue of the SPEAKER, Dr. H. A. Schroeder surveyed the status of present knowledge relative to the importance and, in some cases, the biochemical function of several elements in man. In view of the interrelationships of soils to plant composition and animal and human nutrition, a review of current research dealing with the distribution of these elements in the environment would seem to be a natural corollary to the previous article. Because of the immense scope of this subject, no attempt will be made to present an exhaustive review. Instead, a few important problems will be outlined and the potentials of emission spectrochemistry in this area will be emphasized.

Restricting the discussion for the moment to plants, let us consider what criteria constitute evidence of essentiality of an element. Originally, investigators considered the recurring presence of an element in a wide variety of plant species as sufficient evidence for essentiality. Before long, however, it was realized that plant roots absorb elements rather indiscriminantly (within reasonable limits) from their growth medium. The situation is somewhat analogous to an ion-exchange resin in an aqueous solution of several exchangeable ions. Just as a resin demonstrates selectivity for certain ions but does not totally exclude all others, so plants absorb many elements which are quite likely not essential.

In 1939, Arnon and Stout (1) formulated the still accepted criteria for essentiality as follows: "an element is not considered essential unless (a) a deficiency of it makes it impossible for the plant to complete the vegetative or reproductive stage of its life cycle; (b) such deficiency is specific to the element in question and can be prevented or corrected only by supply of this element, and (c) the element is directly involved in the

nutrition of the plant quite apart from its possible effects in correcting some unfavorable microbiological or chemical condition of the external medium." On this basis, an element may demonstrate a beneficial effect on plant growth without being among the list of essential nutrients. Chromium and nickel improved the growth of barley yet they have not been shown to be essential. Exactly how they function is not known. They may have a synergistic effect, or substitute partially for an essential element.

The essential mineral nutrients are usually divided arbitrarily into two groups: the major or macronutrient elements, necessary in comparatively large amounts; the trace or micronutrient elements. In the case of plants, the first group includes sulfur, phosphorus, potassium, magnesium, calcium and nitrogen. Of course, carbon, hydrogen and oxygen are also essential but they are not considered mineral nutrients because they are obtained from air and water whereas the other six elements are obtained largely from soluble compounds in the soil. The essential trace elements are iron, manganese, boron, copper, zinc, molybdenum and probably vanadium and cobalt. Chlorine might be placed in either group because it is generally present in rather large amounts but it is only required in very small amounts.

Demonstration of the essentiality of the macronutrient elements was a comparatively straightforward problem and will not be considered further. For trace elements, however, the difficulties were and, in fact, still are of much greater magnitude. To determine which elements actually are essential, it is necessary to use solution cultures in which the element in question is not supplied in the nutrient medium. Two major difficulties arise here. First, there are often sufficient quantities of

A year after receiving his PhD. from Rutgers University, C. L. Grant has just returned to the University of New Hampshire where he did his undergraduate work. He will be on the teaching staff there as well as conducting spectrochemical research at its Engineering Experiment Station. His principal academic interest is in emission spectroscopy methodology as applied to agricultural and medical problems.

"Contrasting sharply with metallurgy," he says, "the agricultural sciences have not fully accepted emission spectroscopy as an analytical tool. Beset by claims, often extravagant in the face of problems many times more complex than those in metallurgy, agricultural scientists have tended frequently to view with skepticism spectrographic results, preferring the traditional, established, individual-element methods of analysis." Dr. Grant hopes to help counter this feeling not only by continuing his own significant researches but also by encouraging competent people to enter the field. Here he expects to contribute first-hand by establishing a course in practical spectroscopy slanted towards agricultural matters.
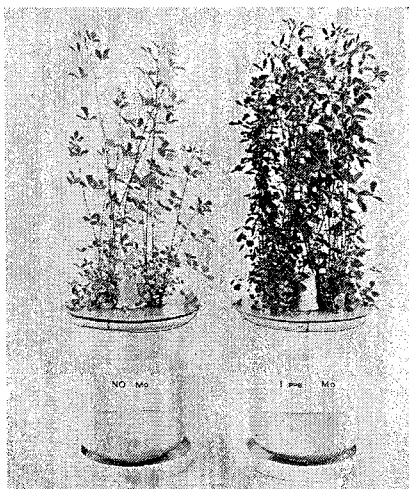
these metals present as impurities in the macronutrients making it necessary to resort to painstaking purification techniques before deficiency can be induced. Secondly, there may be a sufficient supply of the element in the seed to carry a plant through a complete life cycle. To circumvent this, it may be necessary to carry plants through two or three generations before deficiency symptoms appear. Arnon has pointed out that, for this reason, it is helpful to use a test species having a high requirement for a given micronutrient.

The study of molybdenum deficiency symptoms in several species, reported by Peterson and Purvis (21) illustrates the above points. Grown in solutions freed from molybdenum by double coprecipitation with copper sulfide as a carrier, normal corn seeds produced full size plants although some evidence of deficiency was present. Grain from two of the ears from plants receiving no molybdenum contained 0.01 and 0.015 ppm. while none was detectable in a third ear. Seeds from this third ear were planted again in a "molybdenum free" solution culture. Here, the seeds which did germinate produced distorted seedlings which died within a few weeks.

MOLYBDENUM DEFICIENCY

The effectiveness of as little as 1 ppb. of Mo in nutrient solutions is shown by the growth differences of Atlantic alfalfa.

(Courtesy of H. J. Evans, E. R. Purvis and F. E. Bear, Plant Phys. 25, 555; 1950)

At first glance, the study of seventeen or so elements in the soil-plant complex would not appear to pose a problem of too great magnitude, once their essentiality has been demonstrated. However, when one considers the great variability of soil composition and physical and chemical properties, the diverse nature of fertilizer practice, climatic variations, the widely varying nutrient requirements of different species for optimal growth and product quality, and the interdependence of each of these on the other, the enormity of the task is obvious. To complicate matters further, a certain balance among the elements seems to be required; i.e., the optimal concentration of a given element is dependent on the concentration of one or several other elements in the plant. For example, typical iron deficiency symptoms can be induced by supplying abnormally high amounts of manganese relative to iron. The first symptoms of iron deficiency generally occur in the young leaves and consist of a yellow mottling of the interveinal areas. If the deficiency persists, the yellowing continues until it eventually encompasses the whole leaf. It is frequently difficult or impossible to interpret plant analytical data for any single element without data on several other elements. In such a circumstance, the utility of multi-element emission spectrochemistry is quite obvious.)

One further aspect deserves special mention. Although elements such as nickel, chromium, lead, cadmium, titanium, aluminum, strontium, barium, tin, selenium and others do not meet the criteria of essentiality, their determination may often be just as important as the essential ones, for several reasons. Many elements exhibit toxicity effects, either in the plants themselves or in the animals that consume these plants. Crops such as alfalfa, lettuce and spinach are very sensitive to soluble aluminum in acid soils (the roots degenerate) whereas blueberries, potatoes, and several other crops are quite tolerant to high levels of this element. Paradoxically, this particular toxicity effect is believed by many to be the result of phosphorus deficiency induced by the precipitation of immobile aluminum phosphates in the plant tissue. Be that as it may, the determination of aluminum is thus of value as a diagnostic tool. An example of toxicity to animals is that of selenium which is prevalent in plants used by grazing animals in some Western states.

At present there is much disagreement on the best approach to the evaluation of the nutritional status of crops. No one argues about the desirability of being able to predict directly from a soil analysis the fertilizer requirements of a crop. In general, however, this has not as yet proved feasible for trace elements. Since it is well known that the various forms in which nutrients occur in the soil are absorbed by plants with different degrees of facility, much attention has been given to devising methods for extracting "available" nutrients from the soil. The soil is leached with various solutions in the hope of matching plant uptake. Although a few workable generalizations of this type have been developed for some macronutrients, much less is known about the trace elements for many reasons, not the least of which is analytical detectability. The successful accumulation of such information for trace elements will be aided by knowledge of the solubility of many compounds in several solvents as well as the release and resorption rates of these elements from minerals to a soil solution. One disadvantage of chemical extraction techniques is that they cannot reproduce the conditions under which the plant, growing in the field, absorbs nutrients from the soil. Such methods then depend upon empirical correlation of extractable quantities with plant uptake and yield as determined by field trials. Therefore, each crop requires calibration for each element; even then these calibrations will only hold within certain environmental restrictions.

Of course, the major advantage of this approach is that it allows one to *predict ahead of time* what the fertilizer requirements of a crop are likely to be when grown on a given soil.

The other common method of attack is that of plant tissue analysis. Even here the establishment of standard values of sufficiency or deficiency for various species under varying conditions is a tremendous undertaking. Bradford and Harding (3) found up to 50-fold variations in the minor-element contents of orange tree leaves sampled from high-yielding orchards with apparently normal trees. In addition, there is frequently much debate over the proper tissue to sample, the proper time of sampling, etc. A further disadvantage is that for many plants, the effects of an inadequate supply of a trace element may not be manifested until after considerable growth has occurred and the damage may never be completely repaired. However, quick recovery can sometimes be achieved through the use of foliar sprays. At the present state of the art, plant analysis rather than soil analysis must be considered the more highly developed approach for trace-element diagnosis.

Twenty years ago Cholak and Story (5) pointed out that the spectrochemical analysis of biological materials involves more problems than most metallurgical analyses because the former show greater inherent compositional variations for a given type of material. For example, the cobalt content of plant tissues may range from 0.02 ppm. or less to 50 ppm. or more—a 2500-fold change. They further stated that concentrations of inter-

est in biological substances are commonly 10-100 times less than in metals. Today, the last statement is no longer true when one considers the contamination levels of importance in many high-purity metals such as germanium. Nonetheless, biological analysis is still more complex than the analysis of pure metals because of the highly variable matrix of the former. The matrix must be made uniform from sample to sample, generally by diluting with a pure material such as lithium carbonate. This naturally reduces the sensitivity by the dilution factor, often to a value beyond detectibility of the element being determined. The contention, expressed by Cholak and Story, that a proper understanding of all factors involved in the chemical preparation of samples is as essential as an understanding of the spectrographic technique used, still appears valid.

The use of spectrochemistry in agricultural and biological research has, until recently, been retarded also by the relatively high cost of equipment. Furthermore, early investigators were not cognizant of the need to study several elements simultaneously. Where only one or two elements are to be determined, colorimetric or polarographic methods represent a better choice than emission spectrochemistry, except in a few instances. During the past ten years, progress in basic knowledge of mineral nutrition plus the increasing availability of research funds has enabled many people to obtain the requisite instrumentation. In view of the well documented economy of spectrochemical analysis on a cost-per-element basis when several elements are determined, this should represent a sound investment. Unfortunately, this expectation has been realized in too few instances.

A shortage of personnel thoroughly trained in spectrochemistry made virtually inevitable an associated rapid increase in the number of people who became "part-time spectrochemists," but who remained primarily interested in the elucidation of the fundamentals of mineral nutrition. Experience suggests that these people have often been unable or unwilling to refine methodology at a desirable rate. As a result, the whole concept of spectrochemical analysis has been the object of much unjust criticism by many researchers in the life sciences. In view of the frequent use of purely empirical and over-simplified methods, this criticism as a generalization seems to be unwarranted. It should not be inferred that no good methods for the analysis of agricultural and biological materials are available. On the contrary, some excellent procedures have been developed and used by a few workers, but even these may yield poor results if the principles underlying them are violated by untrained people.

What can be done to improve this situation? Two approaches would appear to be possible. The category of researchers whom I have classified as "part-time spectrochemists" often have a rather sketchy background in optics, atomic physics, electronics and frequently in inorganic chemistry. The statement above is in no way intended to belittle such people because knowledge in these areas is generally not their responsibility, i.e., they are experts in other areas. Furthermore, their interest in spechtrochemistry is primarily related to the interpretation of results rather than in the detailed procedure of obtaining the data. Nonetheless, in light of the personnel shortage, the availability of an adequate training program at some university or institute could help these people immeasurably. Such a program should stress the areas of deficiency mentioned above through a practical rather than a highly theoretical approach. In addition, the analytical chemistry of trace-element separations etc. should be covered. It must be emphasized that one or two week indoctrination courses are woefully inadequate to satisfy this need.

Another approach would be to enlighten more people trained primarily in chemistry and physics to the research potentials in the life sciences. It has been the writer's experience however, that many competent spectrochemists tend to look with disdain upon such problems as the determination of cobalt in *grass*. There seems to be a "who cares" attitude. In view of the predicted world population explosion and the nutritional requirements necessarily associated with it, we had best learn to care. What I am indicating, then, is that the responsibility for improvement must be distributed across several disciplines. Let's pull together.

One of the major needs is for methods possessing proven reliable accuracy. It should be noted that I have specified accuracy rather than precision or both, primarily because the latter has usually received greater emphasis in methods development. Furthermore, the requirements for precision in the analysis of biological materials are generally less stringent than in metallurgical analysis. The rationale for this statement is based on the fact that uncontrollable biological variability usually makes a greater contribution to the total variability than does a good spectro-chemical method of analysis. Nevertheless, improvement in precision should remain one of our goals; any modification to improve precision which can be accomplished without undue reduction in the range of applicability, or increase in the complexity of a method, is of significant value.

In addition, a high accuracy is required to provide more efficient and reliable comparison of data from different laboratories. The problem would seem to have two major facets. The lack of primary standards is a severe trouble-spot. Incidentally, X-ray fluorescence, colorimetry and related techniques are plagued by the same difficulty. The preparation of standards and methods (for leaf tissues for example) and the establishment of standard values through analsyes by several laboratories is beset by many difficulties. Among these, sample decomposition and heterogeneity and the lack of agreement in analytical data from different laboratories are particularly significant.

The report by Kenworthy et al. (11) illustrates the problems mentioned above. Twenty pound samples of leaves from four kinds of fruit trees were collected, dried, ground, mixed and distributed to several laboratories for analysis. Results for macronutrients showed reasonable agreement but this was not so for minor elements where most coefficients of variation were about $\pm$ 30%. Somewhat surprisingly, the largest coefficient was 77% for sodium, for which individual laboratories reported values from 22 to 1300 ppm for the peach leaf sample. Thus, although individual methods may have yielded very precise values in a given laboratory, there was serious bias between laboratories. Despite the unsatisfactory results in this attempt, hope for success in such a program should not be abandoned as yet.

Synthetic standards of unquestionable composition, are an obvious starting point. In this connection, solutions have a decided advantage with respect to homogeneity, a property that is difficult to retain with powder standards which are sometimes prone to fractionation on standing because of particle size and density differences and electrostatic effects. However, the major failing of synthesized standards has been the lack of a sufficiently demanding requirement for properly conducted recovery experiments. Too many recoveries are performed by adding a known quantity of the inorganic form of an element after the original sample has been wet or dry ashed. Results of such studies frequently give a favorably biased recovery value. The writer would prefer to see more recovery experiments in which a radio-tracer is incorporated into the living biological tissue, preferably through assimilation by normal metabolic processes.

The radioactivity of such samples can then be monitored throughout every stage of the chemical processing with the tracer initially present as part of the usual organic complex. Having demonstrated repeatable quantitative recovery from chemical processing, synthetic inorganic standards may be quite reliable.

Another area which should not be neglected is detectability. As biochemical separation techniques are refined, greater and greater demands for trace-element data on micro-samples will be required. With very small samples, matrix modification and trace-element concentration will no longer be tenable.

Perhaps the most extensive high calibre studies of spectro-chemical methodology have been conducted at the Macaulay Institute. Many readers are undoubtedly familiar with the concentration procedure developed several years ago by Mitchell and Scott (15). This carrier precipitation procedure, using 8-hydroxyquinoline, tannic acid, and thionolide with aluminum and iron carriers, is effective in isolating many trace elements from matrices of alkalis and alkaline earths. The isolated precipitate is analyzed, after ashing, by a direct-current arc using either cathode-layer or conventional anode excitation.
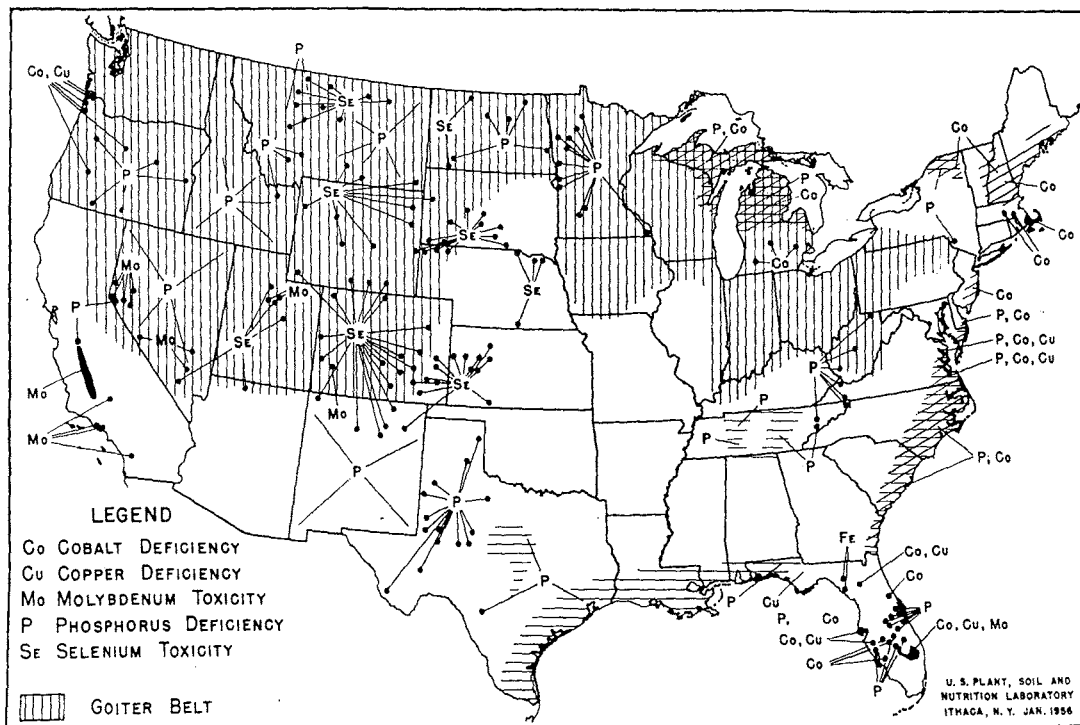
Scott (23) has recently reported on very promising results obtained with a direct-reader. Soil extracts are excited by the porous cup technique while plant ash is briquetted with a 1-1 mixture of potassium and calcium sulfates, graphite, and cellulose powder and excited as a rotating disc. Others who have reported good success with spark excitation are Kenworthy (12), using a rotating disc technique on solutions of plant ash, and Paolini and Kennedy (20) using the same technique on homogenized, unashed food products. Pickett and Dinius (22) have studied extractable trace elements by a procedure in which dithizone is used to isolate certain elements. The dithizone extract was then concentrated and analyzed in the graphite spark.

Progress in the explanation of the relationship of certain mineral deficiencies and/or toxicities in plants to various di-

sease states in animals has led to a demand for maps showing the geographical distribution of these conditions. Mitchell (16), working at the Macaulay Institute for Soil Research in Scotland, stated that "the more important factors which ultimately determine the amount of any trace element supplied to the grazing animal through the herbage are: (1) the total content in the soil and in the parent material from which the soil was derived, (2) the portion of the total content capable of being utilized by the plant and (3) the relative uptakes of the various herbage species concerned." He further indicated that the ease of constructing maps depends on the nature of the area. In Scotland, where the bedrock geology is complex rather than uniform, the factor of prime importance is generally the soil parent material, although local soil conditions cannot be disregarded. By utilizing information on the factors controlling the distribution of trace elements in rocks, Mitchell feels that one can predict, with some accuracy, the likely level of the total trace element content in any soil. However, local pedologic factors must be taken into account. For example, poor drainage has been found appreciably to increase the amount of extractable trace elements. Some areas of almost complete infertility have been found to be associated with excessive contents of extractable nickel. This situation was greatly improved through the application of lime. As a matter of fact, most trace elements become less available as soil pH is raised by the addition of lime. Molybdenum is a notable exception to this rule.

Oertel (19), after conducting a statistical study involving soils from Queensland, Central Australia and Tasmania, reached conclusions somewhat at odds with those of Mitchell. In Oertel's opinion, the relation between the concentration of a trace element in a soil and in its parent rock is often not close enough for satisfactory estimation of the former from the latter. Further study may clarify this point.

In this country, considerable progress in the mapping of deficiency areas has been made by workers at the U. S. Plant, Soil and Nutrition Laboratory in Ithaca, New York (7, 13, 22).

LEGEND
Co COBALT DEFICIENCY
Cu COPPER DEFICIENCY
Mo MOLYBDENUM TOXICITY
P PHOSPHORUS DEFICIENCY
Se SELENIUM TOXICITY

||||| GOITER BELT

U. S. PLANT, SOIL AND
NUTRITION LABORATORY
ITHACA, N. Y. JAN. 1956

Known areas in the United States where mineral-nutritional diseases of animals occur. The dots indicate approximate locations where troubles occur. The lines not terminating in dots indicate a generalized area or areas where specific locations have not been reported.

Extensive areas of phosphorus deficiency and several areas of cobalt deficiency have been plotted. In addition, it has been reported that many of the young, excessively drained soils of the Coastal Plains and the Northeast as well as areas of alkaline soils in the West, are deficient in several trace elements. Areas of selenium toxicity have been delineated.

Study of trace elements in major element fertilizers has produced valuable results. Bingham (2) has shown that western-produced phosphate fertilizers contain 5-fold more zinc than the comparable eastern-produced product. Clark and Hill (6) compared the amounts of manganese, copper, zinc and molybdenum in rock phosphate and processed phosphates and suggested that present day superphosphate manufacture incorporates copper and zinc from corrosion of equipment. Although producers were understandably skeptical of this inference, unpublished results obtained in the writer's laboratory on several processed fertilizers indicated the presence of rather large amounts of nickel and chromium which might have come from corrosion. The question would seem to merit a closer look under controlled conditions.

Another aspect of several fertilizers is their ability to modify the uptake of minor elements, increasing some and suppressing others (14). Intensity of fertilization and type of fertilizer appear to be important factors in the minor element status of plants.

Determination of the proportion of an element that has been taken into a plant from applied fertilizers as opposed to natural soil reserves, has been effectively studied using radio-tracer tagged fertilizers. Considering the interactions between elements, radio-tracer behavior might be better interpreted if soil extracts and plants containing the radio-tracer could be analyzed spectrochemically. Work in this laboratory has been concerned with adapting solution residue methods with spark excitation to this problem. Although this technique is ideally suited on the basis of cleanliness, simplicity, low heat production and ease of trapping and monitoring radioactive contamination, several difficulties had to be overcome before satisfactory precision and accuracy could be obtained for a variety of sample types (8).

While so far we have dealt with essential trace elements and their effects on growing plants and animals which consume them, there are other equally important, applications of the emission spectrograph in agricultural research. Cannon (4) has reviewed the subject of geobotanical prospecting in which the presence and analysis of certain plants serve to spot valuable ore bodies. A technique of considerable potential, geobotanical prospecting has already helped locate copper ore bodies in Sweden, uranium ores in the Colorado plateau and underground salt domes which, in turn, cover oil deposits. Spectrographic analyses have been conducted on plants with deep roots extending to the water table to seek relationships between uptake and the existence of ore bodies leached by the water.

O'Connor (18), of the U. S. Department of Agriculture in New Orleans, is planning to describe the use of the spectrograph for determining metals in cotton fibres. Modified to resist stains, wrinkles, shrinkage and to repel water, modern fabrics are treated with chemicals—often metallo-organics—which are readily identified by the emission spectrograph.

Since most agricultural products end up as food, the spectrographer is often called on to measure the heavy and toxic metals to make sure they meet the stringent requirements of the Food and Drug Administration. In the same general area of toxicity, researchers are attempting to remove radioactive strontium-90 from plants or, preferably, to inhibit its ingestion by the plant with some sort of soil treatment. Some experiments are being conducted with non-radioactive strontium, the spectrograph serving as the measuring tool. Another approach in-

volves chelating agents which could selectively remove strontium in the presence of an excess of calcium in animals. At present, although chelating agents for removing many elements are known, one selective for strontium in a calcium environment has not been reported. A good deal of investigation is being carried out especially on milk and its products.

Another interesting application of the spectrograph was made by the author. This involves the job of "labeling" animals from one generation to the next. In order to study the movement of pheasants it would be convenient to have a "tracer" element which could be transmitted from hen to chick. Experiments were conducted with both yttrium and strontium added to the diet (9, 10) of the hen in the hope that, not only would the egg contain a detectable amount of these elements, but the hatched chick would, too. It was further hoped that by using rather high levels in the diet of the parent hen progeny would be tagged up to 6 months of age. Unfortunately, it was found that despite a strontium level five times above normal in the new-born chick, after eight weeks the levels had decreased to normal. Yttrium, on the other hand, was not mobiled like strontium; it was not even transferred to checks in significant amounts. Spectrography was helpful here because both of these elements are difficult to determine by any other analytical methods.

Specht (24) analyzed narcissus plants for mercury to determine their absorption of certain fungicides which, while effective, have a tendency to injure the plant. He found varying pick-up with the strength of the mercurials and also noted a change in the balance of essential trace elements which may have been responsible for the plant damage.

As crops are grown year after year on the same soil with increasing emphasis on its yield per acre, depletion and imbalance of its mineral elements are found to occur. Already, progressive organizations such as the Macaulay Institute are taking steps to "study the rate of depletion of trace element reserves under present-day agricultural conditions so that preventive rather than corrective measures can be taken while, at the same time, avoiding the troubles which can arise if excessive trace element treatment is applied (17)." The ultimate goal is a one-to-one correlation between a spectrographic soil analysis and the needs of the plant, animals and man. While this may be beyond our grasp, much progress towards this goal has already been made and in the years ahead the rate of progress should certainly quicken.
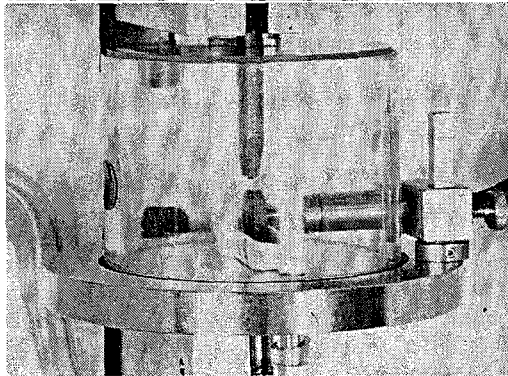
References

1. Arnon, D. Il, The Role of Micronutrients in Plant Nutrition with Special Reference to Photosynthesis and Nitrogen Assimilation in "Trace Elements", Edited by Lamb, C. A., Bentley, O. G., and Beattie, J. M., Academic Press, Inc., N. Y. (1958).
2. Bingham, F. T., Soil Sci. 88, 7 (1959).
3. Bradford, G. R., and Harding, R. B., Proc. Amer. Hort. Sci. 70, 252 (1957).
4. Cannon, H. L., Science 132, 591 (1960).
5. Cholak, J. and Story, R. V., J. Opt. Soc. Amer. 31, 730 (1941).
6. Clark, L. J. and Hill, W. L., J. Assoc. Off. Agr. Chem. 41, 631 (1958).
7. "Factors Affecting the Nutritive Value of Foods" U. S. Dept. Agr., Misc. Pub. No. 664 (1948).
8. Grant, C. L. and Hanna, W. J., Pittsburgh Conference, 1960 (unpublished); Grant, C. L. and Hanna, W. J., J. Off. Agr. Chem. (in press); Grant, C. L., Feb. Meeting N. Y. Section S.A.S., 1961 (unpublished).
9. Grant, C. L., J. Bio. Chem., 235, 2157, (1960).
10. Grant, C. L., Anal. Chem., 30, 401, (1961).
11. Kenworthy, A. L., Miller, E. J. and Mathis, W. T., Proc. Amer. Soc. Hort. Sci. 67, 16 (1956).
12. Kenworthy, A. L., Annual Meeting Soc. Hort. Sci. 1, 1960.
13. Kubota, J., Lazar, V. A., Langan, L. N., and Beeson, K. C., Soil Sci. Soc. Amer. Proc. 25, 227 (1961).
14. Labanauskas, C. K., Embleton, T. W., Jones, W. W., and Garber, M. J., Proc. Amer. Soc. Hort. Sci. 73, 257 (1959).
15. Mitchell, R. L. and Scott, R. O., J. Soc. Chem. Ind. 66, 330 (1947).
16. Mitchell, R. L., Proc. Nutr. Soc. 19, 148 (1960).
17. Mitchell, R. L., Privaite Communication, August 1961.
18. O'Connor, R. T., Private Communication, August 1961.
19. Oertel, A. C., J. Soil Sci. 12, 119 (1961).
20. Paolini, A., Jr. and Kennedy, R. M., Pittsburgh Conference, 1961 (Unpublished).
21. Peterson, N. K. and Purvis, E. R., Soil Sci. Soc. Amer. Proc. 25, 111 (1961).
22. Pickett, E. E. and Dinius, R. H., "Trace Elements in Missouri Soils," Res. Bull. 553, Mo. Agr. Expt. Sta. (1954).
23. Scott, R. O., J. Sci. Food Agric. 11, 584 (1960).
24. Specht, A. W., J. Assoc. Off. Ag. Chem., 168, February 1959.
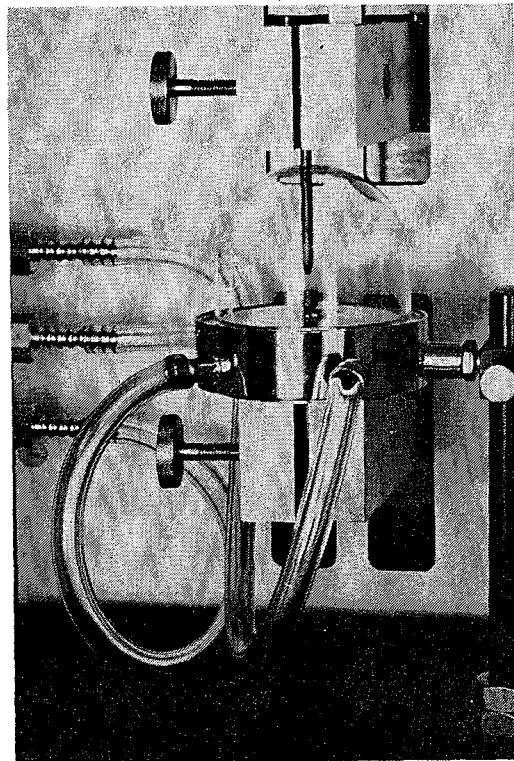25. Thacker, E. J., and Beeson, K C., Soil Sci. 85, 87 (1958).

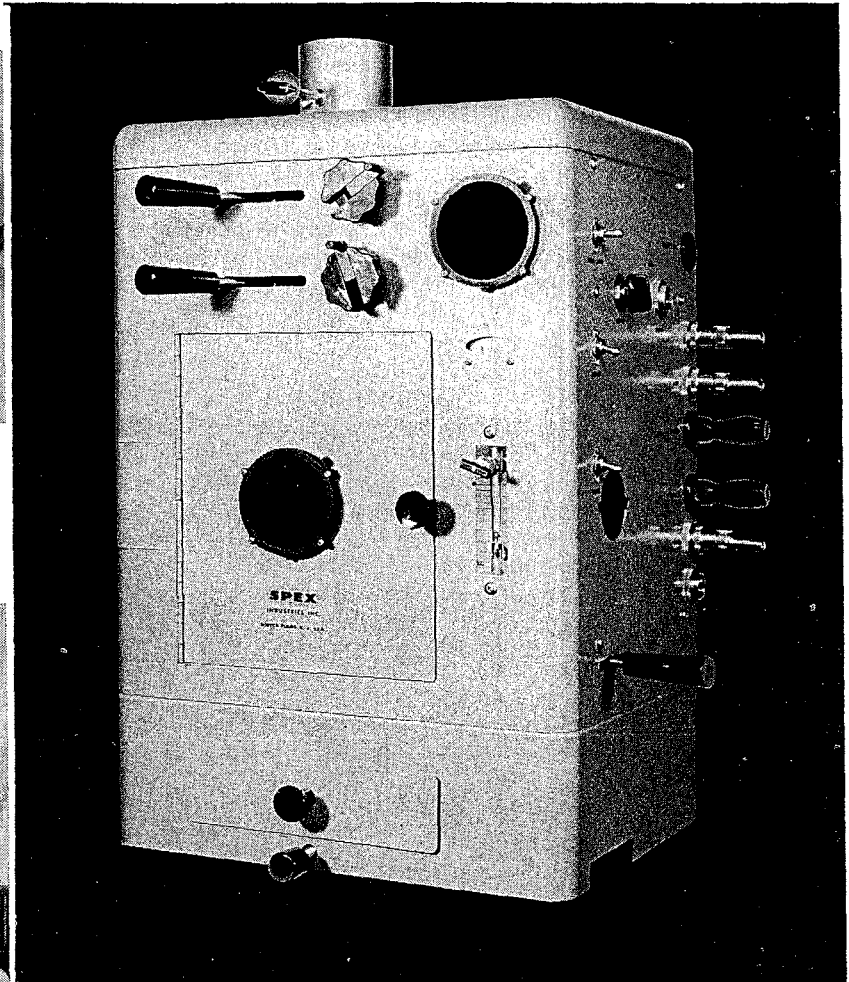*Modernize your Spectrograph with the*

SPEX 9010 ARC/SPARK STAND

VERSATILE

ENCLOSED COMBINATION ANALYZER

STALLWOOD JET

DESIGNED FOR YOUR SAFETY AND CONVENIENCE

* Built-in gauges for water-cooling and air draft.
* 2 built-in motors for rotating samples.
* Bi-lateral, water-cooled electrode clamps.
* 2 variable Polaroid viewing mirrors.
* Erect 4X optical alignment system.
* Filter for exhausting poisonous or radioactive fumes.

RUGGED

* Acid-proof plastic wash-down interior.
* Stainless steel and nylon hardware.
* Rhodium-plated electrode clamps.

··· ADAPTED TO MOST SPECTROGRAPHS ···

SPEX INDUSTRIES INC. SCOTCH PLAINS, NEW JERSEY

tricks of the trade

PREVENTING SAMPLE SPLATTERING IN AN ARC DISCHARGE

Many times the ignition of a dc arc, particularly at high amperage, is enough to splatter the powdered sample from the cup of an electrode. Of the methods used in the past to prevent this, such as putting a thin layer of rubber cement or lacquer over the top of the sample, many are time consuming, messy, and may even introduce unwanted elements. Mr. John P. Walters, graduate research assistant working in the laboratory of Dr. H. Malmstadt at the University of Illinois, suggests the use of our 1/8″ dia. No. 3119 Plexiglas balls which are ordinarily used to mix samples in the Wig-L-Bug. He first packs the sample loosely into a typical undercut electrode, then tamps one of the small balls on top.

"When the arc is first struck," he states, "it usually hits the ball or the edge of the cup near the ball. The heat is enough to melt the ball, flattening it out in the cup over the sample. The arc then centers itself on the melted ball. During the first second or so, the ball volatilizes in preference to the sample below it. Using a 10-12 ampere arc, the ball requires at least five seconds to be completely expelled from the cup. If the electrodes are ignited by touching them, this time may be used to rack the electrodes to the proper operating distance without exposing the emulsion. After five seconds, the arc is usually at equilibrium and the shutter may be opened before the low-boiling elements begin to come off.

"The ease of handling, speed of use, and low expense of the balls make their use routine in our labs."

REFRACTORY ANALYSIS

The spectrographic analysis of refractories is always troublesome because the materials do not conduct an electrical discharge. Mr. Frank De Rose of Coors Porcelain Co. in Golden, Colorado, suggests soaking the material in a semi-saturated solution of silver nitrate beforehand. Dielectric materials such as porcelain prepared in this manner may be sparked successfully. The determination of silver is, of course, sacrificed, but it is not usually of interest in most refractories.

SILVER ANALYSIS WITH THE STALLWOOD JET

Judging from the steeply-rising sales curve of our Stallwood Jets, we must conclude that the accessory is nicely fulfilling the claims of its pioneers. In this connection a recent paper by A. J. Lincoln and J. Kohler (*Technical Bulletin*, Vol. 1, No. 3, Engelhard Industries, Inc., Newark 5, N. J.) is noteworthy. In it the authors show how the Jet has been helpful in improving both precision and sensitivity in the determination of trace elements in silver. With the latest version of the Spex Stallwood Jet, that using a Quartz Enclosure, sensitivities for Au, Ir, Pd, Pt and Rh are increased by a further order of magnitude. This enclosed model (Cat. No. 9025) has the additional advantage of keeping the Arc Stand from being splashed with molten silver.

Material	Am't, grams	Grinding vial*	Time, min.	Results, % —325 mesh	
Alumina, tabular	10	WC	30	100	
Bauxite	3	TS + water	15	100	
Bismuth	5	Plastic Jar & Balls	20	100%	—200 mesh
Bone		AC	10	55	
Boron carbide	7	TS + water	15	85%	—400 mesh
Cement, Portland	20	AC + trichlor	30	100	
Carnauba wax		Plastic Jar & Balls	2	20	
Carbon, activated	10	TS	10	90	
Cereal, dry	10	TS	10	30%	—400 mesh
Corn, dry					
Coal					
Copper shot	2	WC	15	95	
Chromium, slug	10	WC + water	40	30%	—200 mesh
Chromium, ore	15	WC dry	20	32	
Chromium, ore	15	WC + water	20	85	
Ferrochrome	5	WC + water	20	92%	—400 mesh
Grass roots	1	TS + water	10	Paste	
Nickel-Titanium alloy	10	WC + water	20	90%	—400 mesh
Silica sand	5	AC	20	97	
Slag, blast furnace	3	TS + water	20	100	
Slag, open hearth	3	TS + water	20	100	
Ilmenite	5	WC	10	97%	—400 mesh
Titanium diboride	5	WC	10	98%	—400 mesh
Tungsten	25	WC dry	5	65%	—200 mesh
Tungsten	25	WC + water	5	98%	—200 mesh
Welding flux	5	WC + trichlor	30	82	
Zirconium carbide	15	AC + water	30	100	

* AC=Alumina ceramic   TS=Tool steel   WC=Tungsten carbide

TYPICAL GRINDING RESULTS IN SPEX No. 8000 MIXER/MILL

Every so often we pause to find out how some of the hundreds of Mixer/Mills sold are being employed and surprise ourselves with their versatility as well as the ingenuity of their owners. The accompanying chart, while representative, is by no means complete; we would certainly welcome hearing from anyone having unusual applications worthy of telling others about.

8000 Mixer/Mill, 115 v, 60 cy., for mixing quantities of 10-100 ml, grinding 3-25 ml, 1 hour timer, continuously variable jaws holding vials up to 2-1/8″ dia. x 3-1/4″ long, rugged construction and housing, shock mounting ....Each **$330.00**

8001 Grinding Vial. Case hardened steel body with screw-on ends of hardened tool steel, 2-1/8″ dia. x 2-1/8″ long, grinding capacity about 25 ml. With four 1/4″ dia. and two 1/2″ dia. hardened steel balls ....Each **$ 40.00**

8002 Mixing Jar, polystyrene with screw-on plastic cap, 2-1/8″ dia. x 2-1/2″ long, 100 ml mixing capacity..100 **$ 20.00**

8003 Ceramic Vial, made of 99% alumina-ceramic with a 1/2″ dia. ball of the same material, grinding capacity about 15 ml ....Each **$ 32.00**

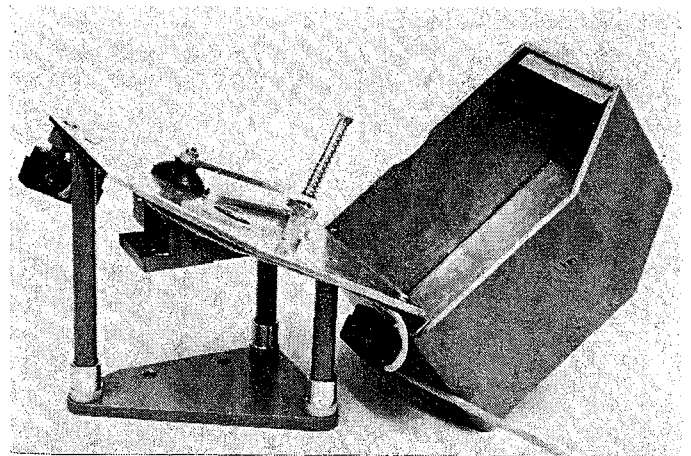Scotch Plains, N. J.

P. O. Box 98

SPEX INDUSTRIES INC.

X-RAY BULK SAMPLE STAND

We are grateful to a number of X-ray spectrographers for calling attention to a safety feature in our No. 3522 stand which is designed for analyzing large samples on General Electric XRD-3 and XRD-5 Spectrometers.

As originally described in the last issue of our SPEAKER, we specified two safety switches in series with each other and with the high voltage to the X-ray tube. In use the X-ray beam would be cut off every time the sample was changed. This might have the effect of reducing the life of the tube and require several minutes of warm-up to permit the tube to stabilize. To correct this, we have added a manually-operated shutter which interrupts the beam in addition to safety switches. The system operates as follows: If the operator closes the shutter first, he can open the hinged lid without causing the beam to be turned off. If, on the other hand, he neglects to close the shutter the safety switch turns off the beam immediately as the cover is opened even a fraction of an inch.

3522 Bulk Sample Stand $475.00

LITHIUM BORATE FUSION TECHNIQUE

For both emission and x-ray analysis, a truly quantitative technique for all sorts of miscellaneous materials has evolved. It makes use of lithium borate which, fused with the sample, converts it to a common matrix both from a chemical and physical viewpoint. (See the article by W.H. Tingle and C. K. Matocha, Anal. Chem., 30, 495, 1958). We are now distributing a high purity lithium borate listed as follows:

6005 Lithium tetraborate, spectrographic grade ..100g. $4.00

1 lb. 11.00

NEW ASTM STANDARD SAMPLES REPORT

The latest edition of an intensive report on standards has been prepared by Robert E. Michaelis. It lists sources of standards, reference and high-purity materials useful in the fields of optical and X-ray spectrochemical analysis. Having grown to well over 100 pages, the booklet well indicates the large number of such materials now available as contrasted with the situation not too many years ago when every spectrographer was forced to shift for himself. The booklet is beautifully organized for the practicing spectrographer. In general, standards are grouped by manufacturer and base metal. They are listed together with the complete analysis and a statement describing their form. A tribute to the thoroughness of its author, the section on pure materials lists 61 sources. The publication is available as Special Publication No. 58-D by ASTM, 1916 Race Street, Philadelphia 3, Pa., at $3.75 to non-members, $3.00 to members.