present (*10*). Superphosphoric acid might be used in conjunction with unconcentrated wet-process acid (32% phosphorus pentoxide) to produce liquid fertilizers.

The acid can be used to advantage in the formulation of granular fertilizers. For example, use of the acid in the pilot-plant TVA continuous ammoniator to produce a 5–20–20 grade gave a higher temperature with the result that granulation occurred at a lower moisture content than when conventional acid or concentrated superphosphate was used. Consequently, the moisture content of the product was lower, and the product did not require drying.

TVA is making limited quantities of superphosphoric acid available to fertilizer manufacturers for experimental use in the production of high-analysis liquid and solid fertilizers.

Acknowledgment

Acknowledgment is made to E. C. Marks, chief, and others of the Wilson Dam Phosphate Branch who supervised the operation of the TVA phosphoric acid plant for the production of superphosphoric acid and to T. P. Hignett, chief of the Development Branch, for his help. F. P. Achorn and J. A. Wilbanks contributed significantly toward development of methods for production of the acid. M. C. Nason and H. W. Elder made studies of the pumping and metering characteristics of the acid. G. L. Crow carried out the corrosion tests. O. W. Edwards made the viscosity measurements. A significant part of the analytical work was done by T. C. Woodis, Jr. The help of Julius Silverberg in the preparation of the manuscript is appreciated.

Literature Cited

(1) Bell, R. N., *Ind. Eng. Chem.* **40,** 1464–72 (1948).
(2) Brown, E. H., Whitt, C. D., *Ibid.*, **44,** 615–18 (1952).
(3) Durgin, C. B., Lum, J. H., Malowan, J. E., *Trans. Am. Inst. Chem. Engrs.* **33,** 643–68 (1937).
(4) Farr, T. D., *Tenn. Valley Authority, Chem. Eng. Rept.* No. **8,** U. S. Government Printing Office, Washington, D. C. (1950).
(5) Giran, M. H., *Compt. rend.* **135** 961–3 (1902).
(6) Huhti, Anna-Liisa, Gartaganis, P. A., *Can. J. Chem.* **34,** 785–97 (1956).
(7) Ross, W. H., Jones, R. M., *Ind. Eng. Chem.* **17,** 1170–1 (1925).
(8) Striplin, M. M., Jr., *Tenn. Valley Authority, Chem. Eng. Rept.* No. **2,** U. S. Government Printing Office, Washington, D. C. (1948).
(9) Striplin, M. M., Jr., U. S. Patent **2,734,596** (Feb. 14, 1956).
(10) Striplin, M. M., Jr., Stinson, J. M., Wilbanks, J. A., "High-Analysis Liquid Fertilizers from Polyphosphoric Acids," Division of Fertilizer and Soil Chemistry, 132nd Meeting, ACS, New York, N. Y., September 1957.
(11) Waggaman, W. H., "Phosphoric Acid, Phosphates and Phosphatic Fertilizers," 2nd ed., pp. 135–143, 158–209, Reinhold, New York, 1952.
(12) Walthall, J. H., Striplin, M. M., Jr., *Ind. Eng. Chem.* **33,** 995–1000 (1941).

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BORON FERTILIZATION

Borosilicate Glass as a Continuing Source of Boron for Alfalfa

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Crop response to residual borosilicate glass and uniformity of boron release from such a glass were evaluated in a greenhouse experiment by growth of alfalfa on Evesboro soil cultures during a second year after treatment. Boron content of the crop was sustained in substantially the same range as that obtained with the newly placed glass in the first year. As application of glass was increased, boron removal by the crop in the 2 years ranged from 142 to 67% of estimated release in the first year alone. Steady release of boron from the particular glass is indicated.

Borosilicate glasses have been studied (*2, 3, 5, 6*) to find slowly soluble materials to effect boron fertilization, especially in land areas of coarse-textured soils and heavy rainfall (*4*). The carrier is used to release boron steadily to compensate for losses from the root zone as they occur during crop growth.

In a 1954 investigation by the authors (*2*), a coarsely ground borosilicate glass frit released part of its boron in Evesboro sandy loam during an 8-month period in which alfalfa was grown. However, the wide variation in response to boron treatment made it impossible to determine whether or not solubilization from the glass had been, in fact, a gradual process. Therefore, alfalfa was grown on some of the cultures again during the following year to evaluate response to the residual glass (boron), and to determine uniformity of release from the glass by comparison of total response in two successive years of crop growth.

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Experimental Procedure

The cultures (7.5 pounds of soil in No. 10 cans) selected for reseeding to alfalfa contained residuals of minus 20-mesh glass No. 176-C. The original additions of glass, which were thoroughly mixed through the soil, were equivalent in boron to 0, 19, 38, 76, and 152 pounds of borax per acre. The soil, after winter storage in an air-dry condition, was moistened, sieved, and mixed individually with the equivalent of 200 pounds of phosphorus pentoxide and 200 pounds of potassium oxide per acre. The pH prior to the application of supplemental fertilizers was approximately 6.0. The amount of boron in the tap water added to maintain adequate soil moisture was estimated to be equivalent to about 0.1 pound of borax per harvest.

Ranger alfalfa was planted on May 20, and harvested four times in the following 7 months. The above-ground portion of the plant was dried at 65° C., weighed, and analyzed for boron by the procedure of Dible, Truog, and Berger (*1*).

Effect of Residual on Crop

Vegetative Response. General growth of the crop varied more than in the previous season. The yields (Table I), in comparison to those of the year before, were roughly one half in the first two harvests, the same in the third, and double in the fourth. There was, also, greater fluctuation in average growth rate (Table II).

Table I. Dry-Weight Yields of Alfalfa at Various Levels of Residual Borosilicate Glass

Glass Originally Added to Soil		Yield in Consecutive Cuttings, Grams/Pot[a]				
Lb./acre	Borax equiv., lb./acre	1st	2nd	3rd	4th	Total
0	0	1.60	1.12	3.82[b]	8.73[b]	15.27
49	19	2.30	1.30	4.57	9.11	17.28
97	38	1.93	1.76	4.67	8.69	17.05
195	76	1.71	1.79	5.05	9.36	17.91
390	152	2.04	1.56	4.02	8.91	16.53

[a] Average of five replicates at zero-addition and triplicate measurements at other levels of treatment.
[b] Deficiency symptoms observed.

Table II. Variation in Rate of Growth Due to Seasonal Factors

Harvest			
Cutting	Date	Length of growth period, days	Average Growth, Mg./Day[a]
1	July 15	56	36
2	Aug. 15	31	52
3	Oct. 13	59	78
4	Dec. 12	60	150

[a] Calculated from oven-dry weight (65° C.) in glass treatments, excluding zero-application.

Yields were usually higher where residual glass was present. However, the differences were not statistically significant at the 5% level.

Visible differences between treatments were not observed in the period of relatively low crop stress of the first two harvests. Deficiency symptoms did, however, develop in the controls in the third harvest, and were present, less prominently, in the fourth. No deficiency or toxicity occurred with any of the glass treatments.

Boron Content. Soil containing increasing amounts of residual glass produced alfalfa containing 22 to 134 p.p.m. of boron. In general the values were a little higher than those obtained in the preceding year, when contents ranged from 18 to 117 p.p.m. with the same levels of the newly placed glass.

Seasonal variation in boron content (Figure 1) was similar to that which occurred during the first year. There was a steady decrease in the first three harvests, followed by a slight increase in the last. The greatest difference in the second year was the failure of boron contents to rise more markedly near the end of the year.

The data suggest that the normal pattern for boron content was modified by large changes in the stress placed by the crop on the available supply. Crop growth was relatively rapid during the latter part of the year when the usual rise in content was not obtained. Average growth rate, yield, and uptake all increased approximately twofold. The reverse of this situation existed in the corresponding period of the preceding year.

Comparison of Average Annual Effects

The over-all yearly influence of the glass is shown in Figure 2 by plotting either average or total response for all harvests in each year against application. This summation excludes variation caused by seasonal factors within the limits of a single season, and conveniently reduces variance due to experimental error.

An increase in yield was obtained in both years up to the 19-pound level of

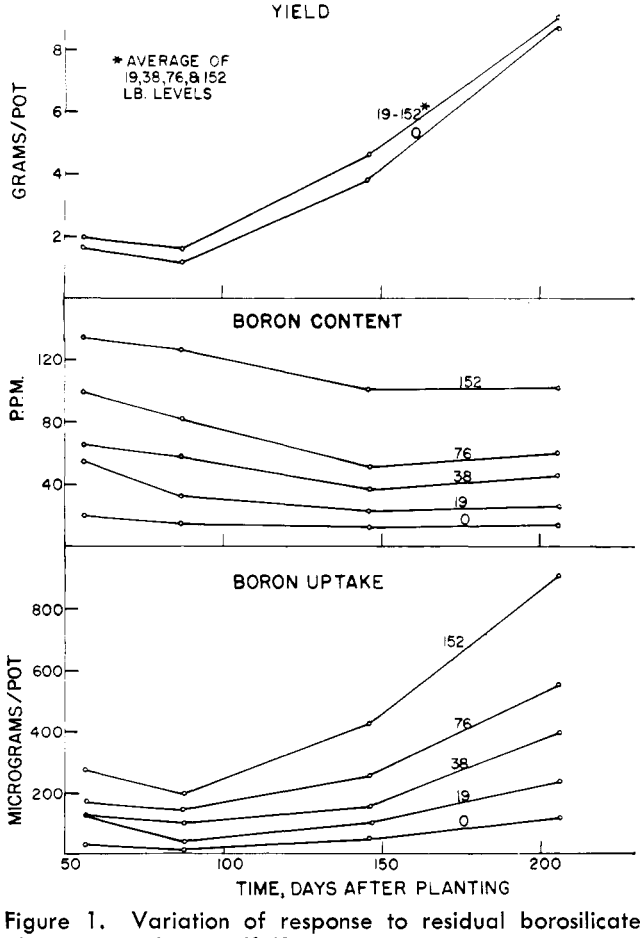

Figure 1. Variation of response to residual borosilicate glass in second-year alfalfa

Numbers on curves indicate borax equivalent of glass application in pounds per acre

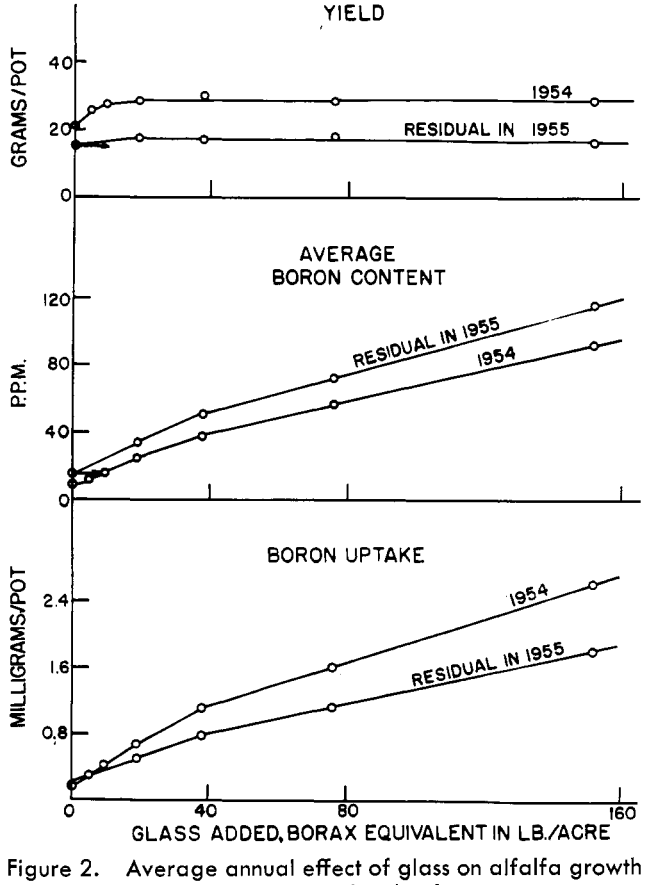

Figure 2. Average annual effect of glass on alfalfa growth and boron utilization at various levels of treatment

Arrows indicate relationship between boron content and yield response for 2 years

glass. Above this point, yield was sensibly constant, though content and uptake continued to increase very measurably.

Average boron content of the crop with the residual glass was actually higher than that obtained with the newly placed glass, at all levels of treatment. This shift, however, was not caused primarily by release of boron from the glass, for an increase of 5.7 p.p.m. of boron was also realized at zero-application (Figure 2). Thus, the relative level attained in the crop was not importantly different with respect to the effect of the glass.

The higher average boron content with the residual may relate in part to an over-all decrease in crop stress. While a rise was appreciated in content, a proportionately larger decrease occurred in total yield. Consequently, there was also a definite decrease in total uptake.

The data for the 2 years demonstrate how sharply vegetative response is defined by certain levels of boron content. With higher boron contents in 1955, the average value for the control was 15 p.p.m. of boron. The same level was reached by the 10-pound treatment in 1954. If the proper displacement is made in yield and content curves so that the yield effect is compared at equal boron contents—as indicated by arrows in Figure 2—good agreement is obtained between yield response of the 2 years.

The range of application in which deficiency is alleviated has special bearing on release from the residual. Critical depletion in boron supply by prolonged crop growth may arise first at low levels of application, where the amounts of boron removed by the crop are proportionately large. This circumstance and the fact that maximum yield was reached with the 19-pound treatment as in the previous year, rather than at some higher level, provide evidence that the available supply had not been reduced seriously.

Estimation of Boron Release. The glass was compared to borax in a parallel series during the first year of growth. Over a comparatively broad but definite range between deficient and toxic levels of boron, yield was sensibly constant and the same for either material. Fortunately, in this region boron content varies with application without any apparent physiological effect on the crop. Thus, within the stated limits the amount of soluble boron, in the form of borax, necessary to produce equal boron content or uptake tends to approximate release from the glass. This quantity of borax will be identified as the "solubilization equivalent" for a given application of glass. The method of determining this quantity is illustrated schematically in Figure 3, wherein the solubilization equivalent, Q_g, for a particular treatment, based on total uptake in six harvests, was 13.7 pounds of borax per acre. Results obtained at different levels of treatment are given in Table III. Release per unit amount of applied boron is given under the heading of Coefficient of Solubilization (f_G) (Table III) to express the relationship in the equation

$$Q_g = f_G \times Q_G, \text{ or } f_G = \frac{Q_g}{Q_G}$$

where Q_G represents the amount of boron in the glass. About one fifth ($C.S._{Av}$) of the added boron was released in soluble form during the first year.

Stability of Supply. The steadiness of supply in the treated soil would depend largely on the relationship between release from the glass and removal by the crop for the conditions imposed experimentally. In Table IV, boron release during the first year is estimated as the coefficient of solubilization average, 0.188, times the various applications of glass. Boron removal by the crop varied from 81 to 40% of the amount of boron estimated to have dissolved from the glass between the 19- and 152-pound levels of addition, respectively. Over the 2-year period the respective removals ranged from 142 to 67% of calculated release during the first year. Similarly, for the 2-year period, removal relative to application was 27% at the 19-pound treatment but decreased to only 13% at the 152-pound level. There was no commensurate decrease in the boron content of the crop or decided curvilinear change in the relationship between content of the crop and application of glass (Figure 2). These results clearly support the view that the supply of water-soluble boron was sustained by the release of significant additional quantities of boron from the residual glass.

Adjustment of Reactivity for Crop Use. A trace element carrier to be suitable for use with a given crop must meet two specifications of performance. First, release of a nutrient must be sufficiently slow so as to extend over most of the growth period. Secondly, for efficient use, release of a nutrient must be substantially complete near the end of the growth period. The test glass appears to meet the first of these specifications satisfactorily and would meet the second for a crop that is to be grown over a very extended period of time by a large application—in keeping

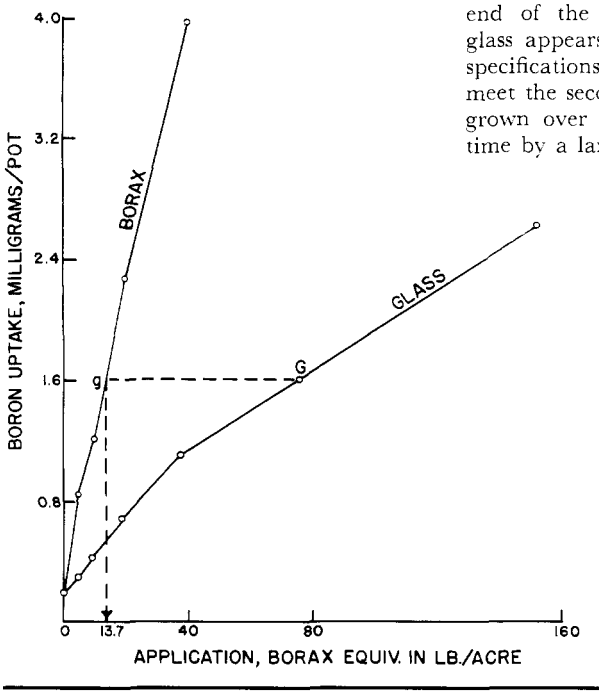

Figure 3. Method of estimating amount of borax needed to equal a certain borosilicate application, with respect to boron uptake by alfalfa

Table III. Estimated Release of Boron from Glass during First Year

Glass Applied (Q_G), Borax Equiv., Lb./Acre	Solubilization Equivalent (Q_g), Lb. Borax/Acre	Coefficient of Solubilization (f_G)
19	3.7	0.19
38	8.5	0.22
76	13.7	0.18
152	24.1	0.16
$C.S._{Av}$		0.188

Table IV. Comparison of Calculated Release during First Year to Annual Removal by Crop

Glass Applied, Borax Equiv., Lb./Acre	Boron Released in First Year ($C.S._{Av}$ × Appl.), Borax Equiv., Lb./Acre	Boron Removed by Crop, Borax Equiv., Lb./Acre		
		1st year	2nd year	Total
0		0.8	0.9	1.7
19	3.6	2.9	2.2	5.1
38	7.1	4.8	3.4	8.2
76	14.3	6.9	4.9	11.8
152	28.6	11.3	7.8	19.1

with the larger losses encountered under field conditions through leaching and the stress of higher yields. To adjust the particular glass for single-season use, reactivity would need to be increased by grinding to a higher degree of fineness.

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Literature Cited

(1) Dible, W. T., Truog, E., Berger, K. C., *Anal. Chem.* **26,** 418 (1954).
(2) Holden, E. R., Engel, A. J., J. AGR. FOOD CHEM. **5,** 275 (1957).
(3) Nestle, K. T., *Glastech. Ber.* **28,** 194 (1955).
(4) Page, N. R., Paden, W. R., *Agron. J.* **46,** 337 (1954).
(5) Rhoads, W. A., Wallace, A., Romney, E. M., *Soil Sci.* **81,** 359 (1956).
(6) Wear, J. I., Hortenstine, C. C., Abstracts, Annual Meetings, p. 29. Am. Soc. Agron., Cincinnati, Ohio, November 1956.

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PLANT ANALYSES

Analysis of Dried Plant Material by X-Ray Emission Spectrograph

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A method is described for determining the concentration of a number of elements in dried, ground plant material using an x-ray emission spectrograph. The concentration of a given element is determined by using the ratio of radiation intensity of that element to the radiation intensity of scatter. Working curves are developed using plant material which has been analyzed chemically. The technique seems to correct for most of the day-to-day variations to which such an instrument is subject. However, a consistent program of daily reference standards is necessary for the satisfactory, continuous operation of the instrument.

RECENT REVIEWS have pointed to the increasing use of the x-ray emission spectrograph as an analytical tool in the fields of metallurgy, ore and mineral analysis, petroleum technology, quality control, and, to a limited extent, in biological assays (*2, 9, 10*). The simplicity of the spectra and the relative ease with which determinations of certain elements can be made suggest its application to the analysis of plant material.

This paper describes a technique which has proved useful for the quantitative and semiquantitative analysis of dried, ground plant material without ashing or concentrating. One of the chief problems in applying the x-ray emission technique is the matter of matrix composition and its effect on the line intensity. The successful use of an internal standard (*3, 8, 11*) and of dilution (*3, 6*) to overcome these effects has been reported. The method reported here uses, in effect, the scatter from the sample as an internal standard. While the basis on which the method developed was different, it is similar to the suggestion of Kemp and Andermann (*7*).

Equipment

A Norelco x-ray spectrograph with an FA-60 x-ray tube is used. The exit port of the sample irradiation chamber is replaced with a $^1/_8 \times 4$ inch Soller slit assembly. For the lower atomic number elements, a helium path, sodium chloride crystal, 0.020×4 inch Soller slit assembly, and No. 62030 GM tube—to detect soft radiation—are used. For the elements of atomic number greater than 25, a lithium fluoride crystal, 0.005×4 inch Soller slit assembly, scintillation counter, and scintillation-proportional unit (a linear amplifier and fast scaler) are used.

The sample holder is modified so that an aluminum alloy frame, 0.05 inch thick, can be slid into the holder and supported along the edges only. The center of the frame is cut out to match the opening in the holder. One side of the frame is covered with 0.00025-inch Mylar film stretched tight and cemented to the frame with rubber cement. The irradiation beam is carefully centered so that no part of the holder or frame is irradiated.

Method

Samples of plant material are dried at 70° C. in a forced hot-air oven for 48 hours and ground in a Wiley mill to pass a 20-mesh stainless steel sieve as previously reported (*5*).

Subsamples are placed in the frame and leveled with the top. Care is taken to distribute the sample as uniformly as possible with a minimum of segregation and packing of particles. It is not necessary to weigh definite amounts of the sample, nor is it desirable to pack the sample into the frame.

For quantitative analysis, the line-to-scatter ratio for a given element—i.e., the angle at which the goniometer is set to receive the radiation from the element being measured—is used as a measure of its concentration. The scatter refers to the radiation intensity in a region free of lines. An arbitrary angle is selected such that the scatter intensity as measured will be as nearly as possible representative of that at the line angle if there were none of the element in the sample. The scatter measures all the factors of the sample other than concentration of the element being measured.

The goniometer is set at the desired angles and the time for a preset number of counts is recorded. These data are converted to counts per second, the line-to-scatter ratio calculated, and the concentration read from the working curve for that element. The working curve is prepared by obtaining similar data on samples of dried, ground plant material which have been analyzed chemically (*5, 12*), plotting the line-to-scatter ratio as a function of the concentration of the element in the plant material and fitting a straight line to the data by the method of least squares.

For semiquantitative analysis, the line-to-scatter ratios are calculated from the intensities measured on the scan and the concentrations read from the working curve used for quantitative analysis. The scans are obtained by setting the goniometer to run automatically over the desired range at 1° per minute and the chart recorder to run at 0.5 inch per minute.

Results

Following the above procedure working curves for four elements were established (Table I). The constants *a* and *b*