

THE PRACTICE known as "soil testing," including chemical analysis and biological studies for characterizing soil fertility, has developed over the past century. During the past 15 years, interest has increased greatly and soil testing laboratories and services have become established and accepted. This has gone hand-in-hand with educational programs promoting more effective use of fertilizers and lime by farmers. Improved analytical techniques and equipment have increased the precision of determining small quantities of elements and make soil testing possible in routine laboratories.

The history of testing soils and the underlying principles have been excellently discussed by Bear (1) and Peech (10) and will be only briefly mentioned here. Nor will biological methods of evaluating soil fertility be considered. It is the purpose of this paper to discuss the chemical methods in use today in this country and, briefly, the principles upon which these methods are based. While it is recognized that one of the very important aspects of a soil testing program is interpretation and recommendation once the soil test values are obtained, no attempt will be made to go into the various approaches used in establishing correlations between soil tests and crop requirements for nutrients.

Analyses commonly conducted in soil testing laboratories include pH or lime requirement, and phosphorus, potassium, calcium, and magnesium in the so-called "available" state. Some laboratories include determinations of organic matter, nitrogen in various forms, and certain of the trace elements.

Soil Acidity

Acidity, the first test used routinely, is still the property most widely determined. Instruments, involving the use of the glass electrode, have made pH a simple and precise measurement.

The pH value for a particular soil is not a fixed factor, but depends on the soil-solution ratio used in its determination; and even with a fixed ratio will fluctuate with season, stirring, and other factors, as discussed in detail by Reed and Cummings (12). In general, a narrow ratio of soil to water (1:2 or less) is used for providing an accepted figure for the pH value of the soil at any given time.

Mineral Element Determinations

Early analyses of soils for total content of elements did not indicate needs for fertilizer or lime. Attempts were made to get some measure of



While well-developed laboratory equipment makes pH determination precise, simple color tests are used in the field for general indications

the rate at which these elements moved into solution, or became "available." Hence, the major problem has been to devise extracting solutions and methods to measure availability with perhaps secondary emphasis on determining the elements once they are in solution.

Early work in England was based on attempts to simulate the action of acids secreted by root hairs which it was assumed had a dissolving effect on the soil particles. This use of weak solutions of citric, oxalic, and other organic acids later lost popularity in the U. S. In retrospect, some of the data obtained, although empirical, did show relationship with known crop-producing powers and fertilizer needs of the soils and were well advanced for their time.

Later strong acids came into use to dissolve the zeolite minerals, believed to be the chief source of the available mineral elements in soils. For some years constant boiling hydrochloric acid (Specific gravity 1.115) was used. An "official" method of the AOAC based on its use was shown to have little foundation.

At one time, considerable effort was devoted to obtaining and analyzing "natural soil solutions," as a method of characterizing soil fertility. Some

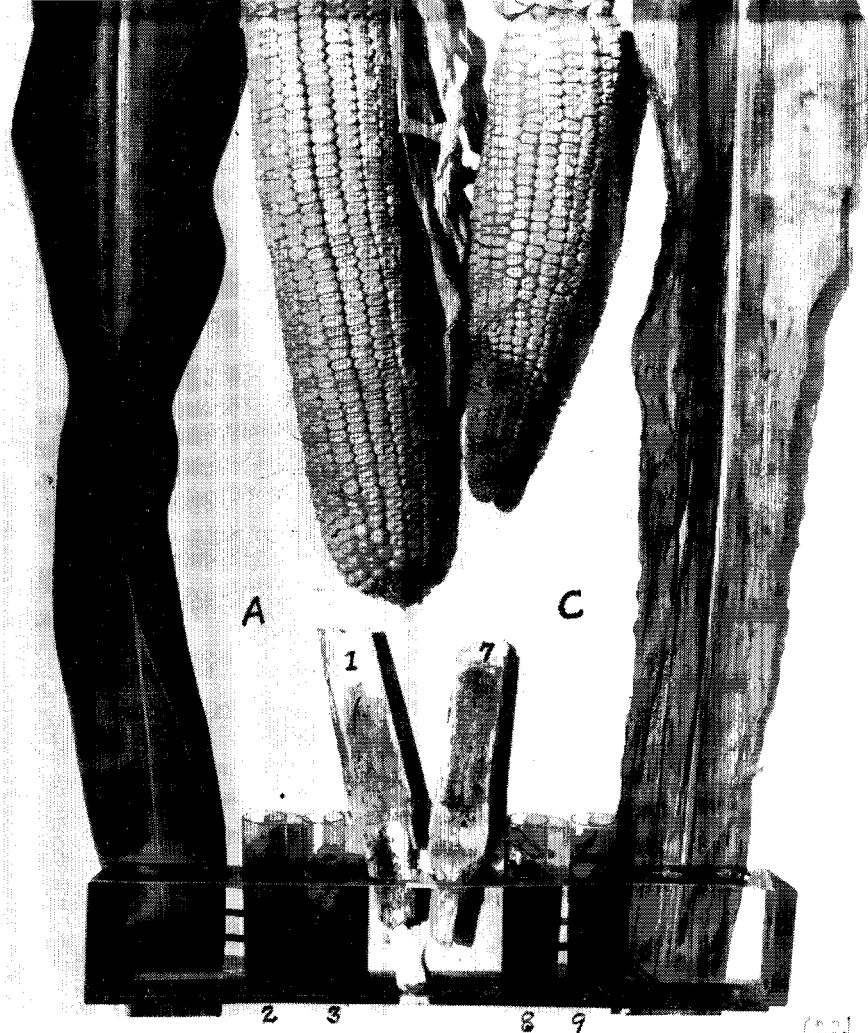
very fundamental information was produced, but the results did not serve their purpose in fertility characterization. Analysis of the filtrate from a soil suspension containing little or no soluble electrolytes will not give the true ionic composition of the natural soil solution.

It becomes obvious that (1) there were difficulties associated with soil solutions and (2) total analysis or strong acid extractions failed to measure adequately the available supply of a nutrient. Hence, agricultural chemists have used empirical methods to extract from the total supply of a nutrient a fraction that is proportional to that part which the plant can utilize during its growing period. In the case of cations such as potassium, calcium, and magnesium, this has often involved the determination of all or a part of the "exchangeable" cation. In the case of phosphorus, weak acid or salt extractions are generally used.

Determining Exchangeable Cations

Since Thomas Way of England reported his discovery of the phenomenon of base exchange in soils, chemists have used this property as a basis for characterizing soil fertility.

The "cation capacity" is defined as



Tissue tests do not measure quantitatively, but often are valuable guides in diagnosing deficiency symptoms. Deficient plant at right shows very high nitrate, very high phosphate, and low potash

the sum of all the exchangeable cations and is usually expressed in milliequivalents per 100 grams of soil. Total *exchangeable bases* refer to the sum of the metal cations (such as potassium, calcium, magnesium) plus ammonium, but exclusive of hydrogen, and the *percentage base saturation* is the percentage of the exchange capacity which is made up by the exchangeable bases.

Determining the exchangeable cations involves replacement with a concentrated salt solution or a dilute acid or the use of electro dialysis. The process of cation exchange is rapid, reversible, and stoichiometric.

The value for the exchangeable calcium, magnesium, or potassium is often used as a measure of the amount of that element "available" for crop use. The values for exchangeable hydrogen, exchange capacity, and percentage base saturation are used along with the pH value and some knowledge of the predominant type of soil colloid to arrive at the lime requirements of a soil.

Exchangeable calcium is a very useful value in acid soils containing no free calcium carbonate. It includes a large part of the total reserve supply of this element and is a good measure

of the amount of calcium readily available for plant use. In soils containing free calcium carbonate, exchangeable calcium is difficult to determine accurately, but in such soils this is of little concern because calcium seldom needs to be added as a nutrient or to correct acidity.

In mineral soils, only a small fraction of the total magnesium is exchangeable, contrasting with the calcium situation. Some salt solutions and acids, as well as electro dialysis, used for determining exchangeable magnesium may remove appreciable amounts of the nonexchangeable. This may not be serious in estimating available magnesium as some nonexchangeable forms undoubtedly are used by plants. But the method is empirical. The measurement of "available" magnesium is often considered less accurate than that of other elements, partially because of errors inherent in its definition. Field and greenhouse correlation data on it are scarce and the average routine soil testing laboratory has difficulty in determination of small amounts of magnesium.

Potassium is an element determined much more frequently than calcium or magnesium, yet interpretations of available potassium are not without

difficulties. It is not uncommon for a mineral soil to contain as much as 2% total potassium, yet respond profitably to potash applications. Most soil potassium occurs in silicate forms that break down too slowly to release potassium in amounts necessary for growing crops. So while exchangeable potassium is often taken as the best means available of estimating available potassium, it is recognized that conversion from nonexchangeable forms to exchangeable is constantly taking place and that soils differ in their ability to replenish exchangeable potash. Methods of measuring release of the nonexchangeable form have been proposed (13, 14), but have not been adopted for routine use.

Soils Can Fix Potassium

The reverse of this process of release is also to be considered, since soils have the ability to fix in nonexchangeable forms appreciable amounts of applied potassium. Wetting and drying of soils has been shown to influence this. In many soil laboratories, especially those dealing with soils containing certain types of colloid fractions, the degree to which the soil is dried will markedly affect the level of available potassium. Complete air-drying of soils prior to analysis is often practiced, but recent data indicate that with some soils this practice may result in increasing the apparent level of available potassium so that the results are higher than those worked out in the correlation studies with crop yields. It is possible that drying under conditions of controlled humidity may be necessary for obtaining values that can be repeated.

These three elements, calcium, magnesium, and potassium, constitute those cations most frequently determined in soil testing laboratories. Generally these laboratories do not use long and detailed procedures for determining the actual amount of the exchangeable cation, but employ empirical methods designed to estimate a proportional amount of the cation in an exchangeable state. Narrow ratios of soil to extractant are used, short periods of contact by shaking, and relatively rapid methods of determining the element in the extract. In common use as extractants today are hydrochloric acid (0.025 to 0.7 N) and acetic acid (buffered with sodium acetate change). Some laboratories use simple salt solutions rather than acids. In using any of these extractants intended to remove a fraction of the exchangeable cation, it should be pointed out that the fraction of a particular cation removed is not always

fixed, but depends on the nature of the complementary cation and of the soil colloid itself. These factors have been pointed out by Mehlich and Reed (7).

The fact that a fixed fraction of an exchangeable cation is not removed by these extractants is not necessarily an objection to their use, for in the presence of the growing plant, something of the same situation exists and it is with plant growth and response that these methods are standardized.

Determining Readily Soluble Phosphorus

Phosphorus exists in the soil in both inorganic and organic compounds. The inorganic compounds include the calcium phosphates and the iron and aluminum phosphates. There are a number of different compounds of these elements with phosphorus, some of which are readily available for plant growth and some that are extremely insoluble. Phosphorus is also held in the soil or fixed by the silicate clays. This is often referred to as "sorbed" phosphate since under certain conditions some of the phosphorus thus held is subject to replacement by other anions and may be plant available.

Phosphorus occurs in the soil in many organic phosphorus compounds and this fraction may comprise more than half of the total soil phosphorus. Some of these compounds are available to plants while others are not. The compounds are quite complex and

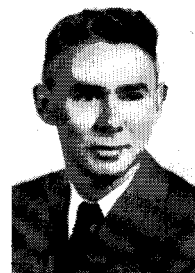
much remains to be done to understand them completely.

It has long been realized that total phosphorus in the soil is of little value in predicting phosphorus response or estimating phosphorus needs of a plant, since much of the soil phosphorus exists in relatively insoluble forms in the soil. While no method has been developed that will predict accurately the exact amount of phosphorus fertilizer to which a given crop will respond, there have been developed empirical laboratory methods that help greatly in assessing the level of available phosphorus in the soil. When standardized against known crop response, these methods are very useful in fertilizer recommendations.

Water, either alone or in equilibrium with known partial pressures of carbon dioxide, has been used. Ordinarily the values for phosphorus extracted by water alone are too low for accurate measurement and the range of values is too narrow for satisfactory standardization. On the other hand, water charged with CO_2 has been in use for some years as an extractant for soils of the West that are often alkaline and frequently calcareous. The nature of this solvent action has been discussed by Olsen et al (9).

For many years dilute acids (hydrochloric, nitric, sulfuric, or citric acid) have been used for extracting soil phosphorus, more frequently with acid soils of the humid regions. Neutral salt solutions of monovalent cations extract about the same amount

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Potash Institute since 1949. A native of Louisiana, he took his B.S. ('34), M.S., and Ph.D. degrees at Louisiana State University in chemical engineering. In 1939-40, he did postgraduate research at Cornell under a Rockefeller

fellowship, returning to LSU as assistant agronomist and professor of soils. In 1942, he accepted a position as agronomist with the North Carolina Department of Agriculture and N. C. State College. In 1948 he became professor of agronomy at N. C. State and director of the soil-testing division of the N. C. Department of Agriculture. Dr. Reed belongs to the ACS, AAAS, American Society of Agronomy, Soil Science Society of America, and the American Society of Plant Physiologists.

of phosphorus from the soil as does water. On the other hand, alkaline salt solutions generally dissolve larger amounts of soil phosphorus from both acid and calcareous soils. Solutions of potassium carbonate have been suggested with the recommendation that this is satisfactory for both acid and alkaline soils. However, the amounts of phosphorus removed from acid soils by potassium carbonate are usually considered greater than the amount available to plants.

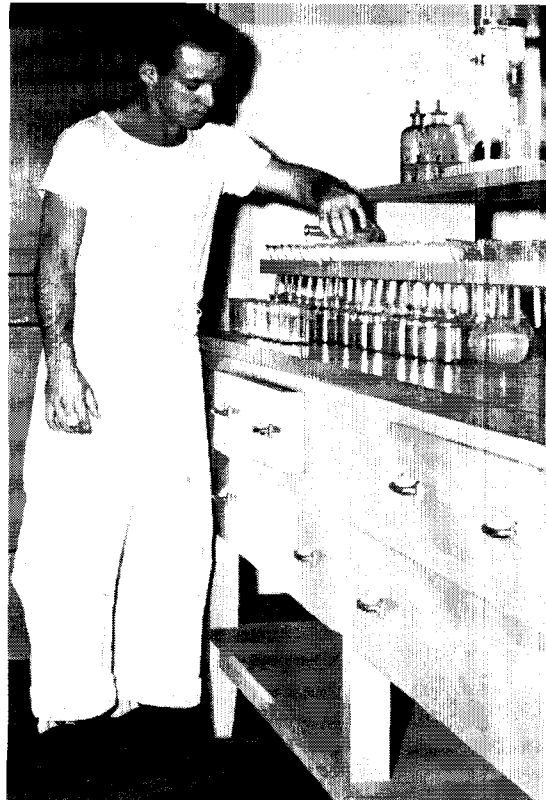
In many laboratories strongly buffered acidic salt solutions are used in routine soil testing. An example is sodium acetate adjusted at pH 4.8 (8) or 5.0 (5). The theory behind their use is that a highly buffered solution would prevent any change of solvent action after prolonged contact with the soil, even if it contains some small to moderate amount of free carbonate. These solutions give clear extracts, and the extract can be used for determining cations also, thus providing a single extract for many available plant nutrients.

Most dilute mineral acids do not extract any appreciable amount of the so-called sorbed phosphate—that portion which is a part of the colloid make-up and which is removed by replacement with another anion. At least a portion of phosphorus so held is considered plant available. It may be determined by replacement with a solution such as ammonium fluoride, sodium arsenate, sodium hydroxide, and certain organic acids like citric.

Today the method outlined by Bray

Samples are received and prepared for testing in N. C. state laboratory at Raleigh





Large numbers of samples often are handled at one time with simple equipment in routine testing laboratories

(2) is widely used for determining available phosphorus in soils, and involves an extractant combining dilute hydrochloric acid and ammonium

fluoride. It is designed to remove from the soil a proportionate amount of the easily soluble and the replaceable phosphorus. A large amount of data, establishing standardization with field response to many crops has made this method particularly useful in the North Central States.

Recently a method for extracting soil phosphorus with 0.5 molar solution of sodium bicarbonate at pH 8.5 has been proposed (9). The extraction mechanism is based on the increased solubility of calcium phosphate as a result of lowering the calcium ion activity in solutions. Also the sodium bicarbonate extracts about one half of the amount of phosphorus on the surface of soil particles, which readily exchanges with phosphorus-32 in the soil solution. The method has been evaluated by use of 212 soil samples from greenhouse and 95 samples from field experiments. An excellent relationship has been established between the levels of available phosphorus determined by this method and the expected crop response to phosphorus.

Nitrogen and Organic Matter Determination

Much of the soil nitrogen useful to plants comes from decomposition of

organic matter, a process influenced by many factors. Estimation of the nitrogen-supplying power of the soil and the need for additions of soluble nitrogen are, therefore, among the most difficult to approach through laboratory means. Over the years soil chemists have attempted this through measurements of total nitrogen, soluble nitrates and ammonia, and determinations of the amount of total organic matter or a fraction of it. It can readily be seen that measurements of total nitrogen would be of little value in predicting nitrogen needs for a particular crop. Nitrate and ammonia nitrogen determinations are also of limited use because of the rapid movement and removal of these constituents and rapid fluctuation from time to time.

Values for total organic matter in the soil mean little in the average soil testing laboratory because of its indefinite composition.

The value obtained is useful in (1) estimating roughly the nitrogen-supplying power of the soil by assumptions as to the proportion of the nitrogen which will become available each year; (2) helping to arrive at the lime needs, especially if exchange capacity has not been determined; and (3) more fully characterizing the soil if

Test kits, used for both tissue and soil testing, have been effective in farm demonstrations, shown earlier, to convey the practicalities of soil testing



the person making the recommendations has not seen the soil, but merely has the soil test data.

Within the past few years, advances have been made in rapid methods designed to predict the nitrogen-supplying power of the soil throughout the growing season. Iowa's soil testing laboratory now includes a procedure (4) that involves incubation of the soil sample at fixed temperature and moisture conditions. Nitrate production during this period is measured, and interpretations in terms of plant needs are based on relationship established through field experiments. A different type of test developed in Wisconsin, (15) is also designed to measure the amount of nitrogen in the soil that will become available for crop growth during the season. It involves soil digestion with potassium permanganate and sodium carbonate. Ammonia is distilled off and measured. This is termed the "organic soil nitrogen that is available," and with this value, directions are given for calculating nitrogen amounts to be added for crops.

Determination of Trace Elements

Most soil testing laboratories do not include routine tests for trace elements, such as boron, manganese, copper, zinc, and molybdenum. From time to time methods have been outlined for these determinations, but field standardization in most areas is not available and there are few data in this country that establish correlations between the value for these determinations in a wide variety of soils and needs.

Manganese determinations, when made, are based on estimates of either the exchangeable manganese or the "easily reducible" manganese oxides when the exchangeable manganese is low. Exchangeable manganese may be obtained by extracting with ammonium acetate and this value may be useful for diagnosing manganese toxicity in acid or poorly aerated soils. If the ammonium acetate contains hydroquinone as a reducing agent, the value is termed "easily reducible" manganese, and this value has been suggested for diagnosing manganese deficiency. Some rapid methods extract manganese with sodium acetate at pH 4.8 (11), and the value is an empirical one that includes manganese in various forms. Its value depends on standardization with field or greenhouse tests.

Zinc and copper occur in very small amounts in soils and determining these elements with precision is difficult in most routine laboratories. Camp (3) and Wear and Sommer (16) have

presented data showing correlations between incidence of deficiency of these elements and the amounts extracted from soils by salt solutions and dilute acids. The possibilities of the zinc test, in particular, should be investigated further.

Boron in the available state in soils can be measured fairly reliably by determining the water-soluble boron. In Berger and Truog's method, soil in suspension with hot water is refluxed for five minutes. While this test appears to be quite satisfactory, very few routine laboratories make any test for boron. Recommendations for its use on crops are generally based on the nature of the crop itself and the soil association rather than on soil test.

Discussion

For any chemical test to be helpful in predicting fertilizer and lime needs, one would expect the extracting solution used in the test to simulate plant roots in their ability to obtain, from the soil, the nutrients required for good plant growth. This is, of course, difficult because this ability varies among plants and even within a plant as the growing season progresses.

As has been mentioned, early chemists approached the subject from the standpoint of determining what constituted the soil solution. Some attempted to define the true solution, others to measure those cations and anions absorbed on the colloid fraction. In soils containing small amounts of soluble salts this distinction becomes difficult to make and is vague. If plant uptake of a nutrient depends on the chemical activity of that constituent, then direct measurement of the ionic activities in the soil, at optimum moisture levels, would appear to offer promise for characterizing the soil with regard to this element. Thus potassium ion activity or calcium ion activity might be determined as we determine hydrogen ion activity with the glass electrode. Development of suitable electrodes has been a problem, but Marshall and his coworkers (6) have explored this possibility and are contributing greatly to the fundamental information along this line. Recently Woodruff (17) discussed the free energy approach to the problem of cationic exchange.

Meanwhile, though empirical, the methods in use today are recognized as very useful tools for characterizing soil fertility and assist greatly in estimating needs for fertilizer and lime.

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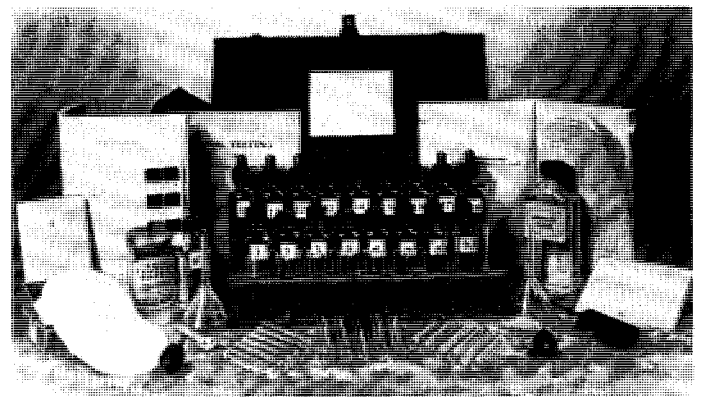


pH meter is probably instrument most widely used in soil laboratory. This model, the Beckman H-2, tests 25 ml. soil with enough water to make a thin mud. Electrode is placed in sample and reading made after 15 to 20 seconds

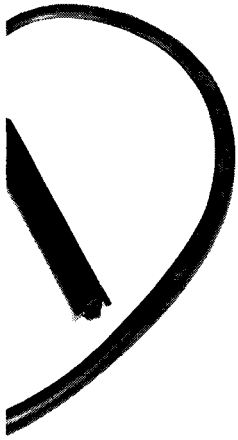


Tools for Soil Testing

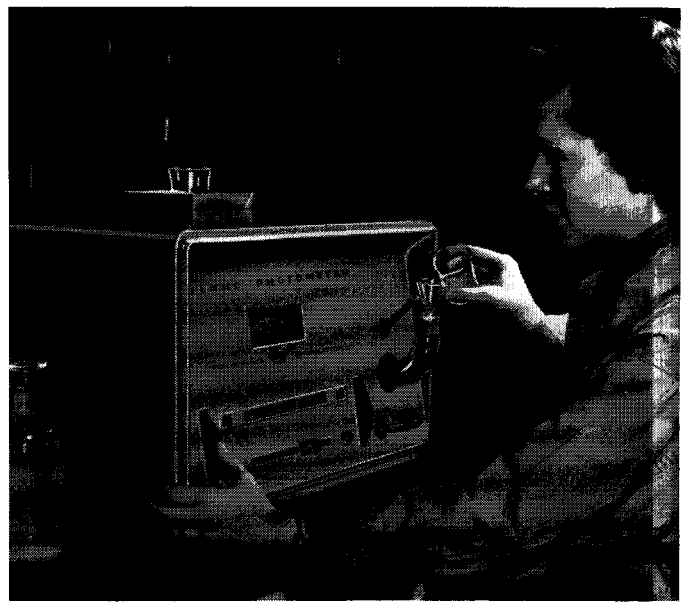
A STAFF REPORT



Test kits such as these from Sudbury Laboratory and Edwards Laboratory are useful in an impressive range of tests. Accompanying instructions often are prepared with aid of state experiment station specialists



Soil tester using wheatstone bridge principle uses a filtered soil extract to indicate total soluble salt content of a soil sample. Model shown is by Industrial Instruments, Inc.



Upper right, flame photometer makes possible large numbers of analyses for fertilizer elements in a short period with high accuracy. Model shown is Perkin-Elmer. Right, junior spectrophotometer is used very widely in soils laboratories of the country. Coleman Instruments, producer of this model, reports 50 in use in a single state

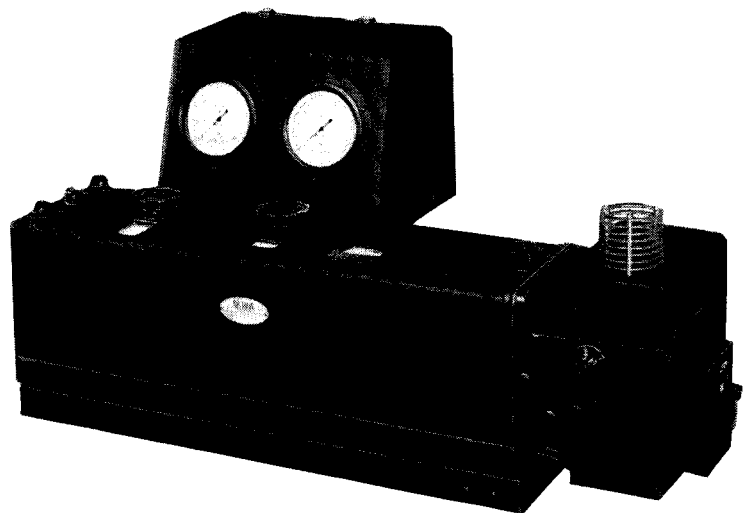


Equipment and information for soil testing are being made better and easier to use. From the farmer to the research man instruments that were mysteries a generation ago are coming into common use.

Kits with chemicals and simple equipment, accompanied by clearly and soundly written manuals, are made useful to operators with rudimentary knowledge of chemistry.

County soil testing laboratories have been aided appreciably by the development of easily used instruments such as electronic pH meters. Small model spectrophotometers have found their way into county laboratories in large numbers.

At the state experiment station and university level, research laboratories depend on high precision and accuracy and use flame photometers and spectrophotometers as well as wheatstone bridges, potentiometers, and radioisotope equipment.



One of more complex instruments used in plant nutrient and soils research is flame spectrophotometer. Beckman model, shown here, rapidly determines traces of elements such as copper, iron, and manganese