of the thiono and thiol isomers were synthesized and their properties compared with the metabolic products of the demeton isomers isolated from plant and animal tissues. An important aspect of this study was the verification of structure and initial purity of these compounds by comparative infrared spectrophotometric and paper chromatographic techniques.

By bringing all of the available techniques of radioassay, paper chromatography, enzyme inhibition, radioautography, densitometry, and spectrophotometry to bear on this problem it was possible to determine the metabolic pathways of the demeton isomers in plants and animals. The principal metabolic pathway of metabolism to toxic metabolites for both isomers is the oxidation of the mercaptosulfur moiety to the sulfoxide and sulfone. A secondary but minor pathway for the thiono isomer may involve the oxidation of the thiono sulfur to produce the phosphate and its sulfoxide and sulfone. Both isomers and their toxic metabolites are degraded by hydrolysis of the P-O- or P-S- bond to form the alcohol and acid. The final proof for this metabolic pathway was the identical comparison of infrared spectra of the synthetic compounds with the metabolites isolated from the plant.

It was then possible to assess the effects of these toxicological and biochemical studies upon the estimation and significance of demeton residues in edible plant materials. The metabolism of the thiono and thiol isomers has been shown to take place in the same fashion as described above. Within one or two weeks after application only oxidative metabolites and hydrolyzed degradation products could be found in orange, apple, and walnut tissues. The thiolphosphate sulfoxide and sulfone are the principal toxic plant metabolites resulting from the pesticidal application of demeton since the thiol isomer and its metabolites have been shown to accumulate from five to 10 times as rapidly as the products from equal rates of treatment with the thiono isomer. The presence of toxic oxidative metabolites should not provide any additional concern in assessing residue hazards resulting from demeton applications since the process of metabolism in animals is identical with that in plants. The animals are therefore exposed to the same toxic processes as the plant, regardless of whether the isomers are ingested in their original or metabolized forms. The hydrolytic degradation of the isomers and toxic metabolites to nontoxic phosphoric acid derivatives is a further safeguard. The estimation of the maximum amounts of toxic demeton metabolites which may be present in plant materials treated with standard commercial dosages of demeton was also reassuring. Average residue values at two and four weeks after application were substantially below 0.1 p.p.m. and generally in the range of 0.01 to 0.03 p.p.m. for orange juice, apple peel and pulp, walnut meat, whole pear, and potato flesh.

These residues are of such low magnitude and their chemistry so complex that they could not have been determined by other than tracer techniques and ancillary instrumentation.

Forefronts of Research and Application

Further developments and applications of these electronic instruments are certainly to be anticipated in this dynamic field. Applications of other presently available electronic instruments are also to be anticipated. For example, vapor fractometry or gas-liquid chromatography will have immediately applications in diffusion studies with fumigants, as in grain storage. Because of limitations in sensitivity of standard thermal-conductivity detectors, microapplications of this technique may conveniently require direct coupling of the chromatographic apparatus with a mass spectrometer or with infrared or ultraviolet spectrophotometers for maximum utility in laboratory scale evaluations of pesticide problems. Nuclear magnetic reasonance spectrometers and Raman spectrometers are still around the corner so far as applications in this field are concerned, although both will undoubtedly be used in the many pressing problems at hand.

As mentioned earlier, the availability now of two spectrophotometers capable of attaining about 190 mμ opens many new analytical possibilities. Theoretically, the region from 185 to 210 mμ is especially interesting in that strong absorption from simple and unconjugated double bonds, as well as from the free bonding electrons occurring in many organic compounds containing oxygen, nitrogen, and sulfur, frequently exists here. This region may find most applications with gases, as solvents adequately transparent from 185 to about 205 mμ are scarce. Water is essentially transparent in this region, however.

It is abundantly clear that the complexity and diversity of the chemical and physical problems currently associated with pesticides research and application cannot possibly be solved without precision instrumentation. The advances in this field during the past decade, as illustrated here, can only portend confidence in significantly greater advances in the future.

A bibliography prepared in connection with this article is available from the authors.

Instruments in

SOILS AND WATERS

M. L. JACKSON, Professor of Soils, University of Wisconsin

PRECISION INSTRUMENTS are making it possible to measure the character of soil and to tailor the needed fertilizer and amendments accordingly. Likewise, water supplies for irrigation can be analyzed quickly by instruments, and proper choice can thus be made of suitable water for irrigation. The soil chemist, with the aid of precision instruments, can make diagnosis of soils and waters for a given crop.

The soil chemist's instruments vary from a simple glass electrode pH meter, conductance potentiometer, and photoelectric colorimeter, through emission spectrophotometers of various kinds, to a radiochemical analysis counter, an x-ray diffractometer, and the electron microscope.

The soil chemist employs precision instruments because they are time-savers; they give more precise information; and they give some specific information not available by any other means.

As a result of the time-saving feature, precision instruments are being increasingly adopted for routine laboratory use. Savings in wages quickly repay the first cost of the instruments and increased precision usually comes along as an extra dividend. For example, the increased objectivity of the modern photoelectric colorimeter is highly worth while aside from mere time-saving.

The instruments that give new specific information are mainly used in more advanced soil chemistry re-

Bausch & Lomb's combination of the colorimeter and spectrophotometer finds widespread application in laboratory analysis of soil and water

search. One example is the study of the crystal chemistry of soil mineral colloids by means of an x-ray diffractometer and electron microscope. Another is the study of the chemical reaction mechanisms of copper and zinc in soils by means of an infrared absorption spectrophotometer. While this type of research is beyond the scope of the routine chemical testing laboratory, results obtained from such advanced studies quickly influence the interpretations made in the routine chemical testing laboratory. For example, x-ray diffractometer findings about the layer silicate, vermiculite, in soil colloids quickly had an interpretation relative to exchangeable potassium analysis done in routine soil tests.

The classification of precision instruments changes rapidly—instruments thought of chiefly in connection with advanced research one year may five years later be in many routine laboratories and still later be considered indispensable in nearly all laboratories.

Precision Instruments Basic to Routine Soil Test Laboratories

Thirty years ago, the soil pH was being intensively studied in research laboratories, as the importance of soil acidity and liming came to be recognized. Measurements were tediously done with a potentiometer attached to the hydrogen gas electrode or quinhydrone electrode. Colorimetric pH indicators were used somewhat. These methods were poorly suited to soil suspensions. Twenty years ago, commercial precision glass electrode instruments were widely introduced into soil chemistry laboratories, replacing the few pioneer home-built and troublesome glass electrode units. Virtually all soil pH testing in the United States is now done by glass electrode pH meters. The soil is prepared for the test by wetting with distilled water to the point of saturation (thin paste) by many laboratories. Some use higher water to soil ratios, and a few use salt solutions for the wetting.

During the period from 1936 to 1946, commercial photoelectric colorimeters came into wide use in soil chemical research. They gradually came to be employed in routine chemical testing of soils for available phosphorus and potassium, and to some extent for calcium, magnesium, manganese, and iron. Photoelectric colorimeters used widely in routine soil chemical testing include the Evelyn colorimeter, based on glass light filters, and the Coleman Junior replica grating colorimeter.

Soluble salts of soils and waters are most effectively determined by electrical conductance measurement with modern alternating electric current conductance (or resistance) meters. Multiplication of the specific electrical conductance in millimhos per centimeter of a water solution by the factor 640 gives the parts of salt per million of solution. The old "salt bridge," which measured the resistance of a soil paste, permitted rough estimates of soil salt content, but a more satisfactory measurement of soil-soluble salts is now determined from the moisture saturation extract of soil.

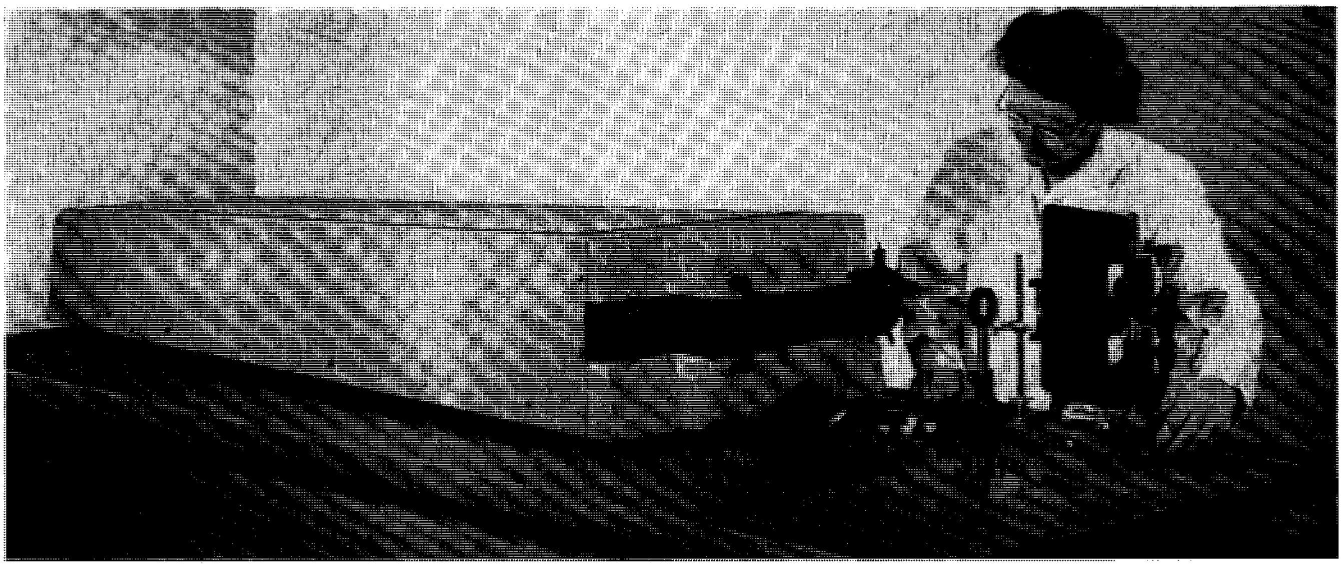
With measurements of specific electrical conductance of this extract, it has been possible to develop a single simple salinity scale for interpretation of salt content in relation to plant growth on soils of all soil textures. Soluble salt measurements in soils and irrigation waters are important in semiarid regions and, because of application of fertilizer or introduction of marine salts, in humid regions also. (Conductance or resistance instruments serve also for measurements of resistance of gypsum blocks used for *in situ* measurements of soil moisture.)

In the past decade, use of commercial flame emission spectrophotometers has developed from research to routine use in chemical testing of soils and waters. First, potassium and sodium analyses were made of extracts from soils and plants and of waters. Calcium and magnesium are now commonly determined as well. The soil is suspended in ammonium acetate solution or other salt solution, then filtered. The determination of the exchangeable metallic cations is made by running the filtrate directly through the instrument. Perkin-Elmer markets a popular double beam flame emission spectrophotometer, based on glass filters. It is employed widely in soil chemical testing laboratories for exchangeable soil potassium. Sodium, and with proper adaptations, calcium and magnesium of waters and soils are also determined. Beckman Instruments markets a popular single beam quartz spectrophotometer used widely in research and in control in soil and water testing laboratories.

Instruments Basic to Soil Chemistry Research

The precision instruments considered in the previous section are also basic to soil chemistry research. Some are used a great deal, others are indispensable although not in constant use. Unique advances on the soil chemical research frontier often follow directly from the application of a new instrument.

Radiochemical analysis of soil and plant material and of waters is car-



Results of fertilizing and spraying programs and general soil management practices can be determined with the Bausch & Lomb spectrograph. Among recent applications of this instrument is foliar analysis to determine fertilizer effectiveness

ried out by means of Geiger counter tubes, either the end-window or the solution-counter type, depending on the element. Effective use is made of the predetermined-count type of scaler. The most simple and first widely employed soil radiochemical analysis was for phosphorus-32 (half-life, 14.3 days). Determinations are made of the percentage of phosphorus in plants derived from the fertilizer and the percentage of fertilizer phosphorus recovered by crops during the first growing season. The amount of soil phosphorus having an availability equal to that in a given type of fertilizer (the "A value") is also determined. The amount of phosphate exposed at surfaces of soil particles and thus available is determined by isotopic exchange. Other radiochemical elements employed in soil chemistry include potassium-42, calcium-45, sulfur-35, carbon-14, iron-55, manganese-54, zinc-65, copper-64, and molybdenum-99.

Spectrophotometers

Arc- and spark-emission spectrophotometers are also well established for the analysis of soils, plants, and waters. Their advantage over the flame-emission type of spectrophotometers is the high temperature of excitation, which makes many more elements determinable than by flame emission. Advantage of emission methods in general lies with the absolutely positive identification of each specific element. Many other methods actually determine groups of elements —for example, oxalate precipitates calcium with a group of elements. Other advantages are suitability for simultaneous analysis of several elements, suitability for very small samples, and rapidity when analysis is to be on a mass basis.

When recording is photographic, arc and spark emission instruments are called spectrographs. Photocell recordings of arc and spark emission spectrophotometers are also coming into prominence. The automatic feature of such instruments and the fact that several elements can be determined simultaneously with results returned on a simple chart make it potentially useful for routine soil and water analysis.

The key to soil colloid structure and chemical identification was provided by x-ray diffraction analysis. Several important soil mineral colloids are layer silicates, the particles of which are plate-shaped. These particles therefore lie more or less parallel when dried on a flat surface. Modern focusing x-ray diffractometers record the diffraction intensity, with a Geiger counter tube, as a function of the angle of diffraction. This type of recorder permits detailed study of spacing sequences along an axis perpendicular to the flat surface on which the layer silicate platelets were dried. Besides ordinary identification of mineral colloid species, a semiquantitative estimate of the amounts present is possible. In addition, a whole area of soil chemical investigations has been made possible by the x-ray diffraction technique. For example, release and fixation of potassium and other weathering reactions can be followed. Build-up of aluminum hydroxide layers between the silicate layers in acid soils has been shown. The process of kaolinite decomposition and phosphate crystal growth due to the addition of phosphate to suspensions of this clay has also been shown.

The electron microscope permits direct observation of the disintegration of the kaolinite crystals mentioned above as reaction with phosphate takes place. Weathering of mica crystals to beidellite has been observed. In various ways the direct observation of the colloid particles has helped with the formulation of numerous chemical reaction mechanisms in soils.

Other Instruments

The polarograph is useful for the determination of zinc, copper, and other elements of soil and waters. Potentiometers are used to measure the oxidation or reduction potential of soil systems, and recent knowledge has made these determinations highly useful and accurate. Also, the activity of metallic cations can now be measured by clay membrane electrodes

MARION L. JACKSON has long been an advocate of applying instrumentation to the problems of soil analysis. Among his contributions in this field is coauthorship of a complete spectrophotometric silicate analysis system. His Ph.D. is from the University of Wisconsin (1939). Dr. Jackson is a member of many scientific groups, an associate editor of *Soil Science*, and a contributor to *Analytical Chemistry*.

which are in many ways analogous to the glass electrode for hydrogen ion activity. The Fisher carbon induction furnace is useful for rapid carbon analysis of soils, giving a determination in three minutes. The mass spectrometer has added further to soil biochemical analysis of nitrogen fixation processes, through the analysis of nitrogen-15.

A Look Forward in Development

The newest addition to the family of instruments used in routine is the flame emission spectrophotometer. It, therefore, is probably the subject at this time for the most significant improvements for soil and water analysis. A recently developed circuit increases the sensitivity range for magnesium, manganese, and other elements which are excited only weakly or barely strongly enough for determination with present amplifying equipment of the low concentrations in soil extracts and waters. Better flame stability is needed. Multichannel recording and automatic recording are important new possibilities.

The rotating disk type of electrode, made of carbon or silver, gives the arc or spark emission spectrophotometer the advantage of a continuous source characteristic of the flame type of emission instrument. A newly increased sensitivity is being provided by electrode design of the polarograph, and this will make the determination of copper in soil and water much more accurate and easy. Improved stability of electron tubes and possible use of transistors in various electronic instruments from pH meters on up would cut down on off-duty time for repairs, and in portable instruments extend battery life. Neutron scatter instruments are being developed for the determination of soil water content. Glass electrodes for pH measurement are being made increasingly more sturdy.

Soller slits in x-ray diffractometers have reduced background and improved the diffraction pattern. Mounting of layer silicate clays on flat suction plates has improved the diffractometer results for some samples. Mounting clay particles by freeze-drying and fog techniques has improved the electron microscope pictures of some soil colloids. Commercial X *vs.* Y recorders have improved the ease of construction of differential thermal apparatus, which is highly useful in research in soil chemistry.

Summing up, the soil chemist has an increasingly wide array of commercial precision instruments for soil and water analysis, and these instruments are constantly being improved. He will make more rapid strides in research and public service in measure that effective use is made of these instruments.

Instruments in

FERTILIZER RESEARCH AND PRODUCTION

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MOST FERTILIZERS and fertilizer materials are solids, a fact that precludes use of the many modern precision instruments based on the properties of gases and liquids. Nevertheless, there are a number of important applications of instruments in fertilizer work.

In the early years of the fertilizer industry, the number of raw materials was small and the processing of these materials into finished products was simple. The principal raw materials were ammonium sulfate and sodium nitrate as nitrogen sources, normal superphosphate as the phosphorus source, and potassium chloride as the potassium source. These materials were used for direct application or dry mixed in various proportions to form low analysis mixed fertilizers. Sometimes considerable amounts of inert fillers such as sand were used, which further contributed to low analysis. The application of instruments in these operations and related research work was very limited.

In more recent years many changes have taken place in the industry, which have resulted in more complex products and processes. Some of these changes are as follows:

- Use of nitrogen solutions composed of various proportions and combinations of ammonia, ammonium nitrate, urea, and water. The introduction of the liquid phase in fertilizer mixing increased the possibility of chemical reactions occurring and increased the complexity of the mixing process.
- Use of many new phosphate materials such as triple superphosphate, ammonium phosphates, and nitric phosphates.
- Use of continuous rather than batch operation for many of the newer mixing processes.

The Coleman Junior spectrophotometer and the Model 21 flame photometer. The latter is widely used to determine sodium, potassium, and calcium in fertilizers