Microchemical and Special Methods of Analysis in Communication Research

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Analysis was beginning to take its place as an important branch of chemistry when, in 1828, Wöhler synthesized urea and the Age of Synthetic Organic Chemistry was born, destined to overshadow analysis for nearly a century. When interest in synthesis began to diminish, in the late 1800's, physical chemistry arose to intrigue the chemical mind. The analyst, thus neglected, had to work with apparatus, techniques and viewpoints evolved for other chemical purposes. In 1910 the Austrian Pregl found it necessary to analyze a sample too small for the then available technique to handle. His solution was the invention of a new kind of analysis—microanalysis, the essential features of which are: reduction of apparatus size and of scale of operations to a point commensurate with sample size; development of entirely new techniques, apparatus and chemical reactions specially suited to analysis; and inculcation in the mind of the analyst of the attitude that analytical problems are, in greater or less degree, research problems, and are to be approached as such, with a mind entirely unrestricted by chemical classicism. This article discusses the applications made by the Bell Telephone Laboratories of microanalytical and related special techniques to communication research and engineering.

THE beginnings of chemistry are lost in antiquity. The basic entities of the early natural philosophers, earth, air, fire and water, gradually gave way to the more numerous and fundamental entities, the elements. In the Middle Ages the alchemists concentrated their talents on an unsuccessful attempt to change base metals into gold. Although these men were, with several notable exceptions, charlatans and fakers, they did focus attention on matter and its objective properties. As early as the 5th century, B.C., Thales of Miletus proposed an atomic theory; but it was John Dalton who twenty-three centuries later formulated the modern Atomic Theory which is the foundation-stone of chemistry.

In the intellectual gropings of man, atoms and molecules, in due course of time, became concepts that explained many phenomena. During all these years there has been a search for the single entity of which all matter was made. Prout's hypothesis of the early 19th century named hydrogen as this single elemental substance. By the end of the 19th century and the beginning of the 20th the one element

became charges of electricity, positive and negative.   Today they are
the electron and the positron.   Out of all the earlier concepts slowly
arose the basic idea of chemistry, that the substantial and ponderable
part of the world, matter, composed of solids, liquids and gases, is
susceptible to controlled transformation.

The devising of tests by which various kinds of matter could be
recognized was one of the early accomplishments of the chemist.
Many such tests were used by the ancients.   It was left for Robert
Boyle (17th century), famous for his Gas Law, to conceive identifica-
tion tests as an important branch of chemistry.   Boyle was the first
to use the expression "chemical analysis."   Lavoisier, of French
Revolution era, is credited with having brought about a chemical
revolution, one result of which was "quantitative analysis"—methods
for determining quantitatively the composition of materials.   The
Swede Berzelius, working early in the 19th century, analyzed with
prodigious industry hundreds of compounds, thus laying the foundation
for the quantitative data of chemistry.   In the middle 1800's the
Belgian chemist Stas repeated and extended Berzelius' work, develop-
ing methods and techniques of much greater accuracy.

With the impetus given to it by Stas' work analytical chemistry
might have been expected to hold the center of the chemical stage
during the 19th century.   But in 1828 the German Wöhler synthesized
the substance urea from laboratory chemicals.   Urea belonged to the
vast class of compounds produced by vital processes, and chemists
accepted the dogma that these *organic* compounds could not be other-
wise produced.   Wöhler's synthesis disproved that dogma, and the
great Age of Synthetic Organic Chemistry began, destined to occupy
chemists' minds for about a century.

Since little attention had been given to analytical chemistry during
these years, it became the step-child of the science, useful but not
particularly creative.   The natural result was that it became a stag-
nant, static science.   It had no special apparatus of its own, but had
to be content with the instrumentalities designed for other purposes.
Similarly, no one had made any special search for chemical reactions
particularly adapted to analysis.   Interest in synthesis had also begun
to wane.   Then physical chemistry burst forth to open up new vistas
for the science.

This continued, essentially, until 1910.   In the University of Graz,
Austria-Hungary, the biochemist Pregl labored for years on a research.
Finally he reached a crucial stage of the work.   Before him were a
few small resultant crystals, whose composition it was necessary to
know before further progress was possible.   His analyst told him

that the sample was far too small to analyze. So Pregl faced a clean-cut dilemma: either he must start all over again on his research, work for years more on a larger scale, in order to prepare a larger sample, or some way must be discovered to analyze the small sample in hand. Pregl chose the latter alternative, and in so doing initiated an era of development in chemical analysis that has not even yet reached its zenith, namely microchemistry.

Pregl worked in organic chemistry. Simultaneously another Austrian, Emich, approached inorganic analysis from the new point of view. In this country Chamot, at Cornell, concentrated on chemical microscopy. These three, Pregl, Emich, and Chamot, are properly credited with the invention of what has come to be called micro-analysis; but their many students and co-workers, as well as scores of independent investigators, did and are doing much brilliant work in the shaping of the science to the practical needs of industry and research.

The basic idea of microanalysis is the reduction in size of analytical apparatus to suit small samples. This has shown the necessity of devising many entirely new methods for carrying out common labora-tory operations. Many new chemical reactions have been discovered, on specific search, that have special usefulness in analysis.

The Microanalytical Laboratory at Bell Telephone Laboratories has been established for about seven years. The peculiar nature of many problems arising in communication research and engineering has made necessary the development of many new techniques and types of apparatus. It can be said, in fact, that this laboratory employs a special kind of microanalysis, constituting, for the most part, an original contribution to the science of analysis.

Analysis consists in transforming an unknown material into one or more recognizable substances. These products may then be suitably separated and purified and their quantities measured. Thus weighing, measurement of volume, solution, filtration, washing, evaporation, drying, ignition, distillation, etc., are familiar operations in analysis.

The techniques and apparatus formerly used for these operations, while suitable for the other chemical purposes for which they were designed, were in general ill-adapted to analysis. Apparatus was designed for general utility and manual convenience; that is, to fit the worker's hand rather than the sample. A chemist of the last century would not have thought of using a 1000 cc. beaker to contain 50 cc. of liquid; he would have selected a 100 cc. vessel. But if an analyst had only 0.1 cc. of sample he could find on the shelf no vessel of commensurate size.

Suppose, for example, it is desired to determine traces of heavy metals such as copper and nickel, in a certain plant ash. Because of the disproportionality between the quantities of the elements sought and the size of the apparatus, the errors introduced are large when ordinary methods are employed. Mechanical losses incurred in the many manipulations and transfers of material, over-dilution with resulting incomplete precipitation, contamination both by dust and by substances dissolved from the glass are almost unavoidable. Since the heavy metals represent only a few hundredths of a per cent of the ash, it is obvious that a large sample, perhaps twenty-five grams, is
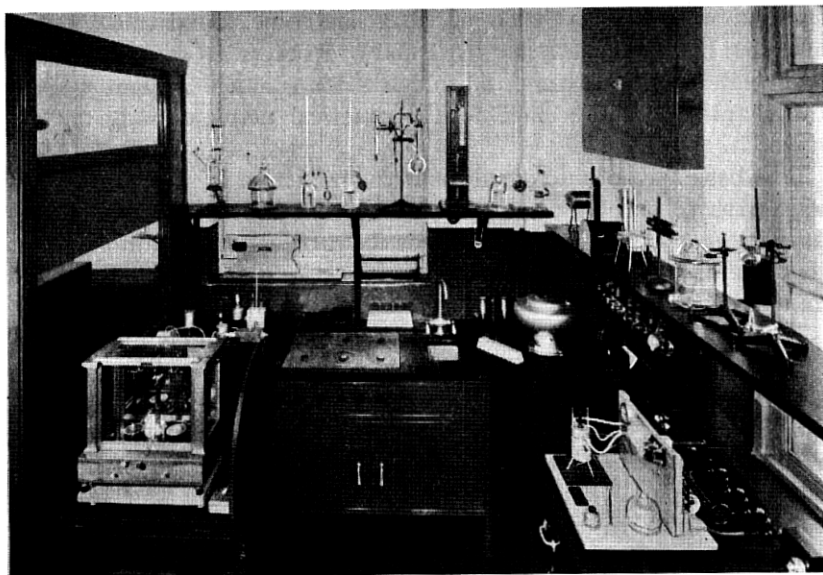

Fig. 1—A corner of the microanalytical laboratory.

required, if an ordinary balance sensitive to 0.1 mg. is used. It would therefore be necessary to start with a kilogram or more of the fresh plant to obtain results which are sufficiently precise.

Other disadvantages of the usual scale of operations are great time consumption, explosion hazards, and costliness of chemicals and apparatus. On a greatly reduced scale, these difficulties frequently tend to vanish. For example, the precipitation of the sulphides of heavy metals is ordinarily avoided wherever possible in quantitative analysis. This is because they are slimy and difficult to filter as ordinarily precipitated with hydrogen sulphide. To filter and completely wash a gram of lead sulphide might be a matter of several

hours and there is great danger that the precipitate will occlude other constituents of the solution. The long exposure on the filter increases the danger of oxidizing the precipitate. On the other hand, a few milligrams of lead sulphide can be precipitated in a sealed tube by a process which produces hydrogen sulphide up to a pressure of ten atmospheres, yet at very little risk of explosion. The resulting precipitate is granular, can be filtered in one or two minutes and its tendency to occlude other metals is much smaller.

Until recently, the most important industrial applications of analysis were the evaluation of raw and finished products and the control of manufacturing processes, neither of which often demanded special technique. With the growing technical trend in commercial production, however, the analyst is being called upon to provide new services. Industrial research must be guided by frequent analyses, both to determine the nature of newly formed products and to gain knowledge of the mechanisms of particular processes. The great diversity of materials, natural and synthetic, and the intricate and often delicate mechanisms embodied in devices of modern manufacture, have enormously enlarged the problem of tracing the causes of failure both in the finished product and in the processes entering into its production. Trouble often arises from obscure defects in materials, the nature of which must be discovered by analytical studies. Impurities, minute foreign inclusions, corrosion and tarnish films, chemical changes occurring with aging or produced as an inherent result of the particular combination of materials used, may contribute.

To make effective use of chemical analysis either as an industrial research tool or as a means of diagnosing manufacturing and maintenance difficulties, the necessity of improving the technique is beginning to be recognized here as in other fields. Great flexibility is needed to fit the operations to highly specific problems. Ability to handle and observe small quantities is frequently necessary because of the minuteness of the phenomena in question. Rapidity is often essential because of the possibility of tying up production, pending solution of the difficulty.

Realization of conventional limitations has stimulated the search for new methods of approach by which the refinement and extension of analytical technique might be accomplished to fulfill the special needs of both science and industry. An outstanding result has been the development in the analyst of a new mental attitude. He seeks to attain his goal first by reducing the scale of operations to a degree consistent with the small quantities of material frequently handled;

second, by augmenting his ability to make observations through the use of adequate instruments; and third, by employing specific and highly sensitive reactions as well as conversion products of high molecular weight.

Micromethods serve the obvious purpose of analyzing minute amounts of material, thereby providing information otherwise unobtainable. Actual experience at Bell Laboratories, however, has shown that the reduction in magnitude of operations frequently permits analyses to be carried out with greater rapidity and more certain results even when the quantity of sample available is not a considera-
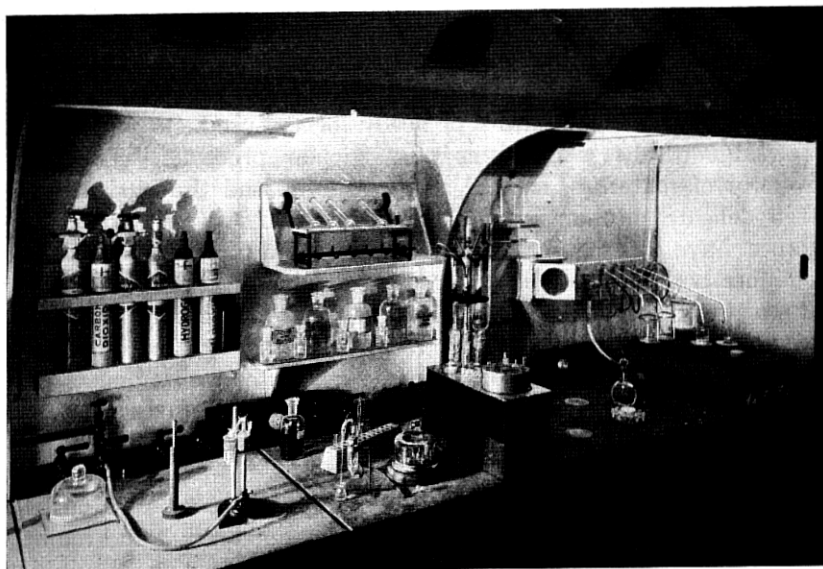

Fig. 2—General view of hood in the microanalytical laboratory, giving some idea of the relative size of glassware and other equipment used.

tion. The construction of apparatus, when more intricate set-ups are necessary, is far easier and more economical on a small scale and the breakage is less. Reactions run their courses more quickly and are more easily controlled. Reagents may be used whose costliness would be prohibitive on a larger scale. These advantages, added to the capacity to make minute observations, provide a technique of great flexibility, a fact repeatedly demonstrated by successful applications to problems arising in the design, manufacture and maintenance of telephone equipment.

In microqualitative examinations, an effort is usually made to bring the unknown material into solution in a volume not exceeding a

few tenths of a cubic centimeter. Identification reactions are then carried out in single small drops of the solution. To accomplish this, a number of procedures are available. One which is very generally applicable, yielding information of a particularly specific and positive character, is that of carrying out the reaction directly under the microscope. By this means, quantities of elements ranging between a thousandth and a few hundredths of a milligram may be detected. The drop to be examined is placed on a glass slide, the reagent introduced from a capillary pipette and the progress of the transformation watched under magnifications of between fifty and three hundred diameters.

In addition to revealing the presence of minute amounts of reaction products separating from the solution, the use of the microscope facilitates study of the individual particles composing such precipitates. A number of properties are thereby brought into analytical significance which might not otherwise be observed or utilized. In ordinary practice, the analyst is guided in his conclusions as to the presence of an element simply by the bulk formation of a precipitate, specific recognition of which is based only on characteristics readily apparent to the unaided eye, such as color and gross structure. Under the microscope, however, the crystal structure and similar distinctive morphological features, color, transparency, index of refraction, behavior toward polarized light, characteristics of growth and other specific properties may all be studied and employed to give greater certainty to the identification. Further, it is frequently possible to identify the individual components of a mixed precipitate, thereby obviating the necessity of separation. Thus, the double salt potassium mercuric thiocyanate gives insoluble compounds with a large number of the bivalent metals. To apply this reagent to a solution containing several metals would result in the formation of a precipitate which to the unaided eye would yield very little specific information. Under the microscope, the experienced analyst, in a single observation, can often tell from the known habits of the crystals produced by various combinations of metals, the nature of the mixture.

Recognition of substances is not always confined to the precipitation of insoluble reaction products, but soluble salts, when the solution is carefully evaporated, sometimes possess sufficiently distinctive morphology to permit direct identification. In this way minute amounts of sodium chloride have been detected in dust deposits collected near the sea-coast. In the identification of traces of organic material, valuable information is frequently obtained from microscopic studies of the crystalline deposits produced when the substance is

sublimed directly on the slide.   Crystallographic constants and other optical properties as well as the melting point and solubility may be readily determined on the sublimate even though only a fraction of a milligram is available.

Another advantage to be gained by reactions carried out under the microscope is that of performing tests *in situ*.   In practice, it is sometimes difficult to isolate physically the particles of material to be studied.   For example, it may be desired to learn something of the nature of a tiny inclusion embedded in a metal or a thin film of corrosion product present on its surface.   Here again, the microscope is of great service, both in guiding the physical manipulations necessary to restrict the action of the reagents to a localized area and in observing the actual identification reaction (usually chosen to yield an intensely colored product or bubbles of gas, rather than a precipitate).

When, instead of the commonly used qualitative reagents, compounds are employed which are capable of more specific and sensitive reactions and which yield intensely colored products rather than precipitates, such products may be instantly recognized, even in a single drop of solution.   Within recent years, many organic compounds have been developed for this purpose.   The use of these, and of a number of inorganic compounds giving highly characteristic color reactions, constitute the basis for a new technique combining rapidity, simplicity, and certainty of identification without the use of the microscope.   The drop to be examined is placed on a white background such as a porcelain plate.   A drop of the reagent is added and the color change, which may involve a sequence of changing shades, is observed. In cases where turbidity is also significant, a black porcelain plate is used. Because of the highly specific nature of these reagents, it is often unnecessary to resort to a preliminary group separation.   Because of its simplicity, the technique is particularly useful for field investigations.

A modification of the drop analysis procedure described above consists in bringing the drop under examination together with the reagent onto loose-textured paper such as filter paper.   The colored product which forms is adsorbed on the fibers of the paper at the center of the drop, while the solution spreads out due to capillarity.   The capillary action of the paper fibers is sometimes utilized to devise rapid separations, thus enabling the analyst to detect two or more elements simultaneously.   In a typical case, a solution contains copper and nickel.   A drop of this solution, acidified with acetic acid, is brought onto the paper which is impregnated with hydrorubeanic acid.   The bluish-black copper compound is insoluble and therefore

forms first, near the center of the drop. The nickel compound, being more soluble, does not form until the solution has spread out to a considerable extent and most of the acid has evaporated, when it is visible as a violet zone near the periphery of the drop.

Papers which have been impregnated with specific reagents and preserved in the dry condition are extremely useful both in the laboratory and the field. In the analysis of gaseous substances or materials readily volatilized, these dry test papers have been very satisfactory. Arsine, stibine, hydrogen sulphide, sulphur dioxide, hydrocyanic acid and other objectionable gases present in minute quantities in the atmosphere, may be detected and their approximate concentrations determined by passing a stream of the air through the fibers of a suitable test paper.

In order to obtain solutions to which identification tests may be applied, some preparatory chemical treatment is necessary. The initial solution and concentration of the sample, its recovery from inert material as well as its separation into convenient analytical groups require laboratory operations capable of dealing with a few drops of liquid and often with a fraction of a milligram of solid. A variety of types of apparatus and special processes have been developed to facilitate these operations. In a few cases, reduction in size has alone sufficed; more often such reduction, with retention of the original form of the apparatus, results unsatisfactorily and new principles must therefore be followed in the microdesign.

For example, it is obvious that the usual folded paper cone cannot be satisfactorily reduced in size to permit the removal and recovery of suspended matter from a few drops of liquid. Microfiltration may be accomplished in a number of ways but the most convenient is to draw the liquid into a capillary pipette provided with a retaining well which holds a very small pellet of the filtering medium. In this way a single drop may be filtered and completely washed in a few seconds, the residue being concentrated in the tiny filter plug from which it may readily be redissolved in a trace of acid. Practically all of the common analytical operations have been reduced to a microscale and may be carried out with rapidity and precision in equipment of appropriate design.

It may be of interest to note here a few of the more ingenious devices and processes that have been developed to aid qualitative microanalysis. The electrolytic cell of H. Brenneis provides for the precisely controlled electrolysis of a drop of solution, at the same time permitting continuous observation of the electrode surfaces under the microscope. By its use, 0.001 mgm. of copper may readily be recog-

nized and as little as 0.0001 mgm. of zinc has been observed on a previously coppered cathode. The electrodes are formed by encasing closely spaced platinum wires in glass which is subsequently cut and polished through a perpendicular plane, thereby exposing cross-sectional areas of the wires. The drop to be electrolyzed is placed on the polished glass surface and the portion covering the platinum areas observed under the microscope.

A process rarely used in ordinary analysis but of great service in microwork is that of sublimation. A few thousandths of a milligram of a volatile crystalline solid may be separated in this way from a
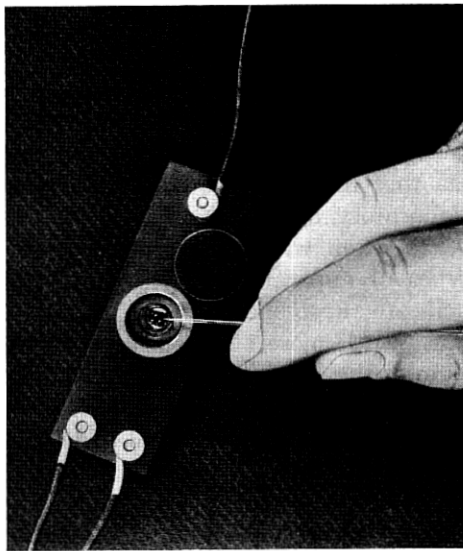

Fig. 3—The electrolysis cell shown here, when used under the microscope, permits one to observe the deposition of metals from tiny drops of solutions. Less than a thousandth of a milligram of copper or zinc may be detected by its use.

large bulk of inert material in a condition that permits immediate treatment with reagents. In order to apply this process to dusts, corrosion products and other frequently-encountered materials, an improved microsublimation chamber has been designed by this Laboratory. The apparatus is so arranged that both temperature and pressure can be regulated. The vapor condenses on a water-cooled microscope cover-glass and the recovery is practically quantitative. As little as 0.002 mgm. of mercuric iodide was found to give a deposit of definitely recognizable crystals.

A phenomenon that has long been familiar, yet not applied to analysis until its value in microwork was recently demonstrated, is

the production of "schleiren" or refraction lines when two fluids of differing optical density are added together without mixing. One liquid is contained in a flat optical cell of a few tenths cc. capacity. The other is slowly introduced below the surface of the first liquid from a capillary orifice. The refraction effects set up are observed through a horizontally mounted microscope under controlled illumination. When one of the liquids is known, such observations are the basis for both specific gravity and refractive index determinations. So sensitive is the method that a difference of 0.0001 in the refractive indices of the two liquids is still detectable. It therefore affords an excellent test for purity. If, for instance, two fractions of a distilled liquid are added together with the production of "schleiren," it may be assumed that the original liquid was not a pure substance.

Glass capillary tubes have shown great versatility in microwork. When the quantity of material operated upon is exceptionally small, as, let us say, in the case of a foreign deposit on relay contact points, their use affords distinct advantages. Almost every operation can be executed through appropriate adaptations of capillary technique. Thus reactions may be carried out under pressure in sealed capillaries when the volume of liquid is only a few thousandths cc. and the whole process watched under the microscope. Distillation and sublimation are processes to which capillaries are especially suited. Suspensions may be centrifuged or filtered in capillaries. In the latter case capillary attraction is the force that draws the liquid through the filtering medium.

The possibilities of capillaries may be illustrated by a practical example. Tiny discolorations were found on the surface of a polished silver sheet used in photocell manufacture. Mercury contamination was suspected and an analytical confirmation was desired. The procedure was as follows: A 1-mm. capillary tube was drawn out to form a pipette having a very fine tip. With this a very small drop of nitric acid was transferred to one of the discolored areas under the microscope, and allowed to act for a few seconds, after which it was removed, transferred to a capsule and the excess acid evaporated. The residue was re-dissolved in a small drop of water and drawn up into a second capillary tube containing a few mm. of No. 32 copper wire. Both ends were sealed and the tube heated in boiling water for a few minutes, after which one end was opened and the liquid withdrawn by means of a finer capillary. The open end was then drawn out to a very fine tube of microscopic bore. The closed end was heated by a microflame, gently at first to drive out moisture, then strongly until the glass had completely fused about the copper wire. Heating in

this manner was continued almost to the constricted portion. When the capillary, after cooling, was examined under the microscope minute globules of condensed mercury were plainly visible. In this process, the mercury is displaced from solution by the copper and
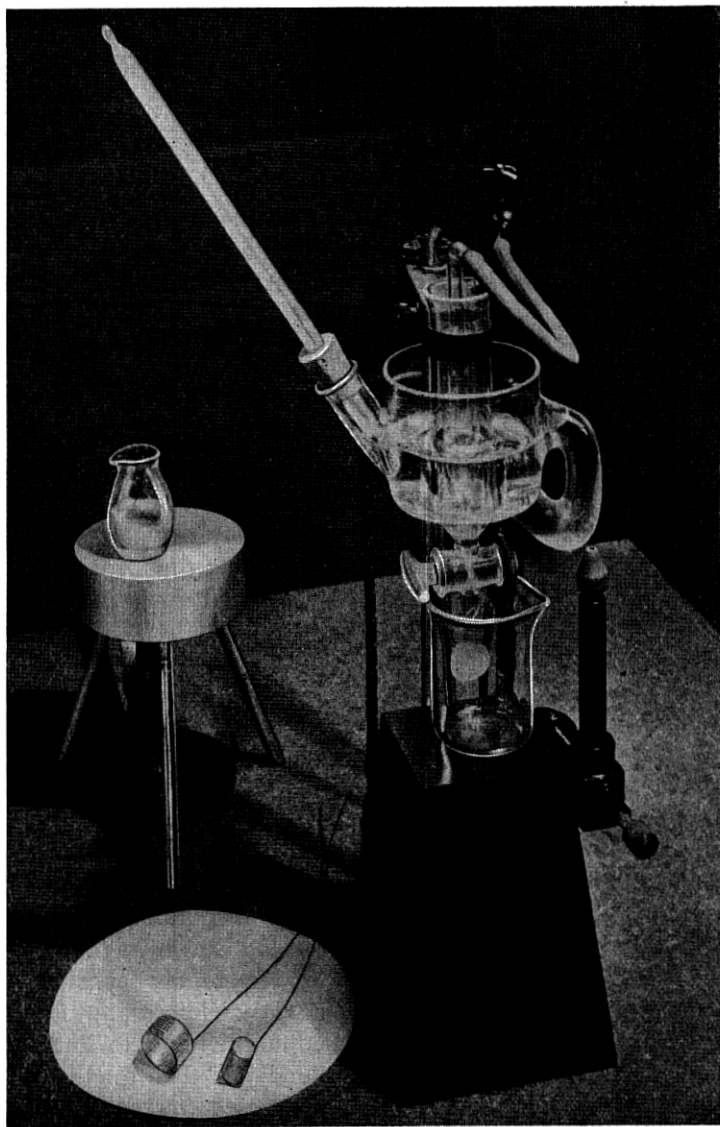

Fig. 4—With this electrolytic cell as little as a milligram of various heavy metals may be precisely determined.

deposits on the wire from which it is subsequently distilled. As little as 0.001 mgm. can be readily detected in this way.

A considerable part of the microanalyst's task is the physical isolation and recovery of the material on which his analytical operations are to be performed. His problems very often require examinations of minute particles or aggregates of foreign substances which have become attached to or embedded in the surface of a material. He may also be required to isolate and study the structural units which compose a given formation. For example, a deposit occurs on the surface of a metal as a result of corrosion. This deposit is not of a homogeneous nature but is built up in successive layers, each of which differs in composition. To obtain a satisfactory picture of the mechanism of the production of the deposit it is necessary to know the composition of each separate layer.

The mechanical manipulations necessary to obtain sample material frequently tax the analyst's ingenuity more than the analysis itself. The work is usually carried out under the low powers of a microscope, preferably of the binocular type. Much of the technique of the biologist has been appropriated by the microanalyst in this phase of his work. Various types of dissecting tools find ready application here. The dental engine with its various attachments, such as drills, burrs, carborundum wheels, has been found extremely useful for drilling out inclusions in metals and for the removal of hard surface films. The micromanipulator, an instrument originally designed by biologists to perform intracellular operations, has recently been employed in microchemical work with very satisfactory results. This instrument furnishes the means of regulating with great precision the movement of needles, capillary pipettes, electrodes, electrically heated platinum wires, etc., under relatively high magnifications. It offers great promise where particles of exceptionally small dimensions are to be studied.

A number of methods have been developed and used by the Laboratories' Microchemical Group for the collection and study of central office dusts. A device which deserves particular mention is the impinger, an adaptation of which has been employed to remove dusts from the extremely localized area represented by a single relay contact point. The device is so constructed that the particles, after being picked up by suction, are projected at high velocity against a microscope slide, the surface of which is coated with an adhesive medium. The slide is removed from the apparatus and the dust subjected to physical and chemical treatment to determine its nature.

In quantitative microanalysis, the analyst is faced with the added

problem of weighing a few milligrams of material with the same precision as might be obtained with samples of the usual size. The Nernst quartz fiber balance, capable of weighing to a few ten-thousandths of a
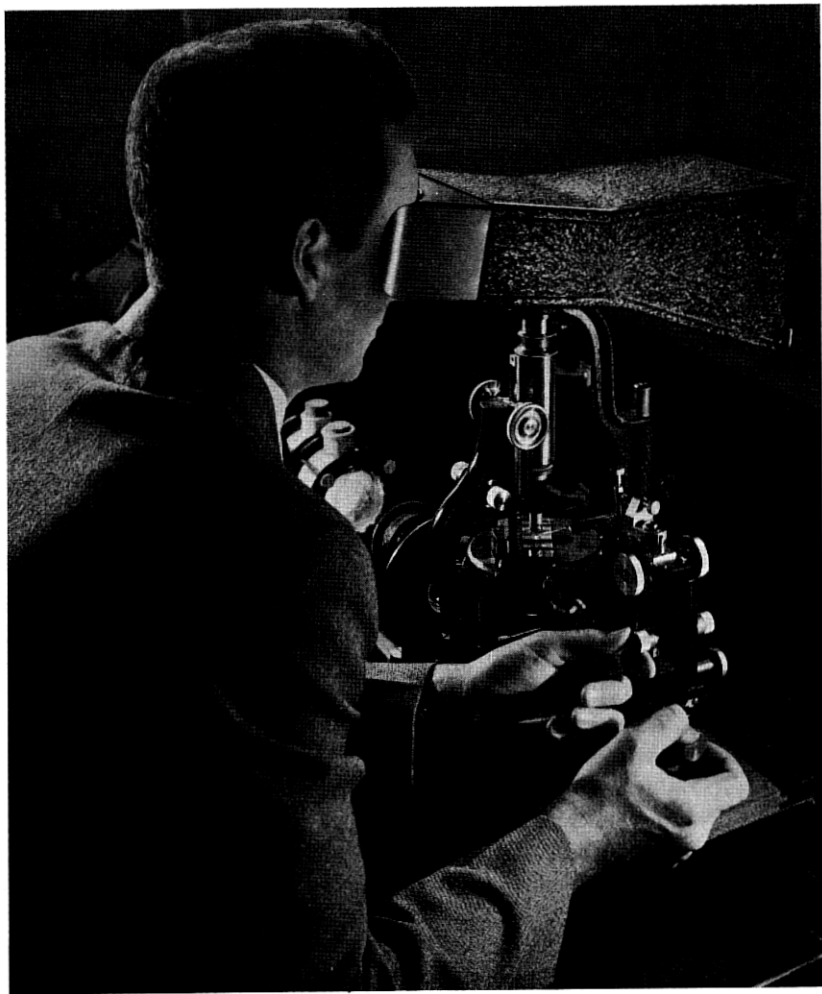

Fig. 5—The micromanipulator finds use when it is necessary to operate on unusually small particles or within areas bounded by the microscopic field.

milligram, has proved very useful in certain types of work, where the total load does not exceed a few tenths of a gram. Its application to chemical analysis, however, is quite limited because of the difficulty of reducing the load to this extent. The quantitative extension of

microtechnique consequently made little progress until a beam balance was produced by W. Kuhlmann of Hamburg, which was capable of weighing to a thousandth of a milligram with no appreciable change in sensitivity with loads up to 20 grams.

With the perfection of this essential instrument quantitative micro-technique developed rapidly, and because of the economy of time and material it is in many cases actually displacing older methods operating on the usual scale. This is particularly true in organic analysis where the methods are ordinarily tedious and expensive. Pregl, who received the Nobel prize in 1923, worked out rapid, precise micromethods for the determination of carbon, hydrogen, nitrogen and various organic radicles, which require only a few milligrams of sample. As an example of the great practical value of such methods may be cited an instance mentioned by Cornwell [1] in which a complex organic com-pound was synthesized with a yield of about a gram of product. The labor and material involved brought its cost to about $5,000. An analysis was required as a check on the composition, and by the usual methods this would have required 0.2 gram of sample at a cost of $1,000. The analysis was actually made by the micromethod on 2 milligrams of sample, cost $10.

Most of the general equipment originally devised to facilitate micro-operations in qualitative analysis is also applicable to quantitative work. Considerable additional equipment is required, however, for the recovery, conditioning and quantitative measurement of the final transformation products of the analytical process. Precipitates are collected and weighed either by centrifuging in suitably shaped vessels or on suction filters which are essentially miniature reproductions of those used in ordinary work. An innovation in filtration practice consists in the use of an inverted filter which is weighed together with the microbeaker in which the final precipitation takes place. The clear liquid and washings are simply drawn off through the filter. This obviates the necessity of completely transferring the precipitate to the filter, thereby avoiding losses that are otherwise almost certain. Duralumin blocks of various designs have been found excellent for drying and conditioning precipitates. The high heat capacity afforded by the large mass of metal insures a very constant temperature. Various types of micromuffle and combustion furnaces have been devised. Their small size greatly reduces construction costs and permits a more generous use of quartz or platinum linings.

For the measurement of liquids, microburettes are available which can be read to 0.001 cc. When the quantities are too small for

[1] Cornwell, R. T., *J. Chem. Education*, 5, 1099–1108 (1928).

measurement by micromodifications of the conventional gravimetric and volumetric methods, the microscope sometimes may be ingeniously applied to quantitative determinations. Colorimetric and turbidimetric measurements may thus be made on a few thousandths of a cubic centimeter of solution contained in a capillary tube. The relative quantities of two or more components of a mixture may frequently be approximated from area determinations made on the individual particles in the microscope field. Instead of weighing the mercury recovered by capillary distillation, the condensed globules may be united by centrifuging and the mass of the resulting single globule estimated from diameter measurements under the microscope. Similarly the analysis of a minute amount of gas may be carried out by measuring the shrinkage in diameter of a single microscopic bubble as the absorption reagents in which it is immersed are changed.

A striking example of a quantitative determination so contrived that the final measurement is performed microscopically is the micromolecular-weight method of Barger. Two solutions, one known and the other containing the unknown, are placed in a capillary with a small air bubble separating them. The ends of the capillary are sealed and the lengths of the two liquid columns measured on a micrometer scale. After several hours the measurement is again made, and repeated at intervals until the column lengths become constant. When this occurs, the vapor pressure of the two solutions will be identical and since vapor pressure is a function of the molar concentration, the latter may also be assumed to be the same in each solution. Knowing the original weight concentrations and the molecular weight of one of the substances, that of the other may be calculated from the change in the volumes of the two solutions necessary to bring about equilibrium.

The application of quantitative microtechnique to engineering and research problems at Bell Telephone Laboratories has required a considerable amount of development work directed toward the improvement of apparatus and the creation of new types of technique. Thus, in order to carry out micrometallurgical analyses, several forms of electrolysis cells were developed which permit the determination of metals such as copper, zinc, nickel, lead, cadmium, tin and others. With these cells, using five milligram samples, the same accuracy is attained as in ordinary analysis on half a gram. One of these cells, designed for the analysis of extremely dilute solutions, permits the qualitative detection of one part of copper, zinc, or lead in 100,000,000 parts of water and is particularly useful in isolating minute quantities

of heavy metal impurities in such metals as aluminum or nickel, or in examining waters after use in corrosion experiments.

In order to reduce the errors of weighing in microgravimetric analysis, it is obviously desirable to obtain transformation products having the greatest possible mass. To facilitate manipulation, it is also desirable to deal only with products of a coarse crystalline nature
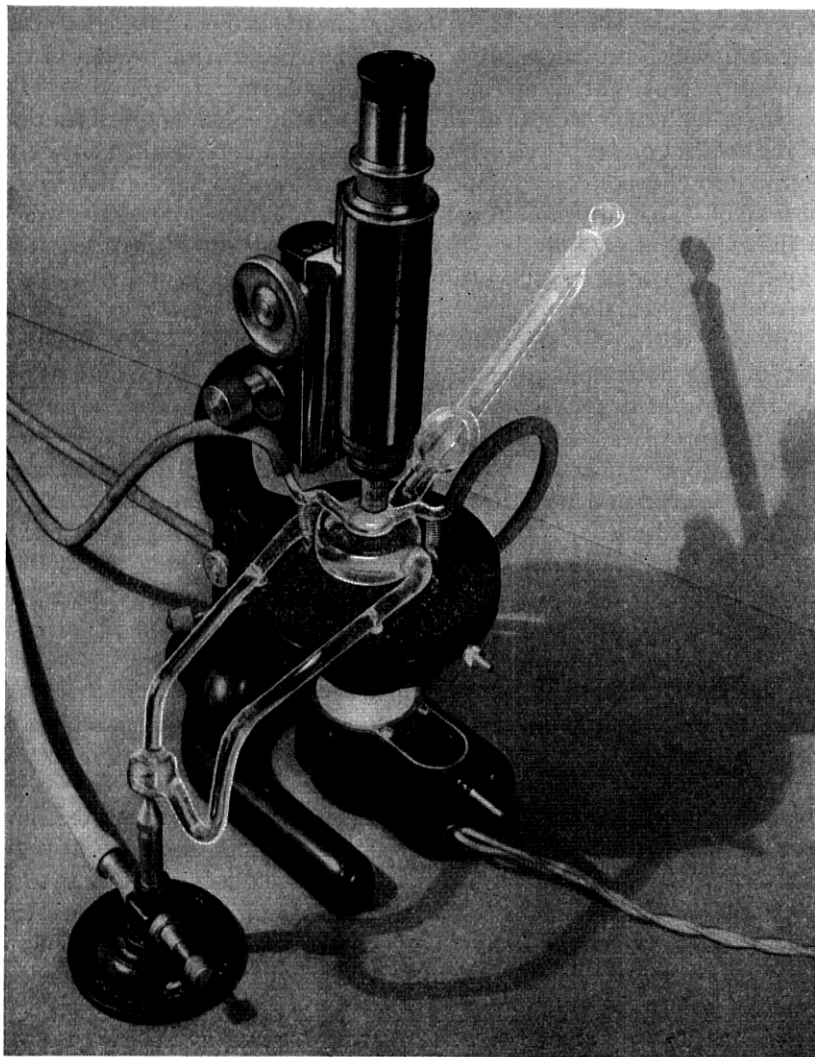

Fig. 6—The glass hot stage assembly shown here provides for the determination of melting points or the sublimation of volatile substances under the microscope.

which may be readily centrifuged, filtered and washed, and which exhibit a minimum tendency to adhere to the wall of the containing vessel. The simple insoluble salts, oxides or hydroxides usually obtained in the older, classical methods, rarely meet these requirements satisfactorily and recently much attention has been given the search for more suitable quantitative precipitants. The result has been an increased use in microwork of organic, complex and double salts of high molecular weight. Thus sodium is no longer weighed as the sulphate, which provides only a threefold increase in the weight of the sodium present, but rather as crystalline sodium zinc uranyl acetate having a molecular weight of 1591 or a weight equal to 69 times that of the sodium present. Silver may be collected and weighed as silver-copper propylenediamine iodide of molecular weight 939. Aluminum, instead of being precipitated as gelatinous aluminum hydroxide, which is difficult to filter, may be separated and weighed as the crystalline oxy-quinolate with an eighteen-fold increase in weight.

Another possibility of chemically amplifying weight consists of employing a train of reactions the final weighable product of which has a high molecular weight. Although it may not contain the element originally sought, this product is still stoichiometrically related to it and provides the basis for quantitative estimation.

Although Pregl, Emich and Chamot are considered the founders of modern microchemistry, there were a number of earlier isolated instances of such methods being used. The earliest attempt to organize qualitative microchemical methods systematically was made by Boricky in 1877 who applied the technique to petrographic studies and wrote a treatise entitled "Elements of a New Microchemical Analysis of Minerals and Stones." In 1885, Haushofer in his book "Mikroskopische Reaktionen" provided a rather complete description of reactions carried out under the microscope, his work covering most of the common elements. It remained for Professor H. Behrens of Delft, Holland, and H. Schoorl to expand the technique to a point where minute quantities of substances could actually be separated and manipulated to permit the application of common analytical operations. In the biological field, H. Molisch developed the technique of applying microreactions directly to plant tissues and in this way was able to identify many intracellular substances. His book "Mikrochemie der Pflanze," and that of Mayerhofer, "Mikrochemie der Arzneimittel und Gifte," are well known.

In Europe, particularly in Germany and Austria, awakening interest in the application of microchemical methods to industrial problems is evidenced by the appearance of a large number of articles on the

subject in current journals. Until very recently, however, American chemists did not appear to have fully realized the technical possibilities and advantages of micromethods. The installation of a completely equipped microchemical laboratory at Bell Telephone Laboratories about seven years ago, constituted, the authors believe, a pioneer step in the direct application of microtechnique in its broadest sense to engineering problems. Since that time, a number of industries and industrial institutions have made similar installations with favorable reports as to their usefulness.

In order to convey a more concrete idea of the types of problems in which the microchemical approach has been particularly helpful at Bell Laboratories, this paper will be concluded with a few actual examples.

The equipment used in the telephone plant and associated industries contains numerous small functional parts, concerning which analytical information is frequently needed. Such information may be desired in connection with laboratory studies required in the design of the apparatus or it may be needed because of unsatisfactory performance in service, traceable to some irregularity in the particular part. Obviously such results as might be obtained by compositing the large number of parts necessary for an ordinary analysis would be inadequate. Both the peculiarities of the individual case and the variations in quality and composition will be obscured unless the analytical study be made to include only particular specimens. Thus single relay contact points, weighing between five and ten milligrams, have been quantitatively analyzed to check the composition of the alloy when excessive deterioration was noticed. The gold plating, amounting to a few tenths of a milligram, has been precisely determined on small areas of handset transmitter parts for the purpose of observing the uniformity of the coating.

In studying the various phenomena occurring in vacuum tubes and photocells the Microchemical Laboratory has frequently been requested to identify and occasionally to analyze quantitatively various metallic films and surface deposits in which the total material has ranged from a few thousandths to one or two milligrams. The distribution of caesium on the various surfaces of the photocell was quantitatively studied by microanalysis, the greatest quantity of caesium present in any one determination being about 1.5 mg. Single filament wires weighing from eight to thirty milligrams have been analyzed, the thoria determined in the case of tungsten filaments, while nickel wires were examined for copper, iron, silicon and manganese.

Micromethods have been utilized in studying variations in composi-

tion between very thin layers of a material. In a typical case, sheets of an iron-cobalt magnetic alloy were observed to undergo a change in properties after rolling to diaphragm thickness. It was suspected that the surface had lost iron through oxidation and subsequent mechanical removal. By using pure silica abrasive, a layer of metal was removed from the surface corresponding to a thickness of about 0.005 millimeter. The metal was then extracted from the abrasive by acid treatment and the iron-cobalt ratio determined microchemically. A similar technique has been applied to tinned copper wire, to determine the quantity of copper dissolved by tin during the tinning process and the extent of its migration to the surface of the coating. It has also been used to study the alloy layer formed between the zinc coating and the iron base in sherardizing and galvanizing processes. Micromethods applied to thin films have been used in the study of the copper-oxygen ratio variation in copper oxide rectifier discs.

The inclusion of foreign particles in the surfaces of metals and other materials occasionally occurs as a result of faulty conditions of manufacture. Determination of their nature and source is naturally necessary before remedial measures can be taken. Since the particles are small, frequently even of microscopic dimensions, microchemical methods in such cases are the only ones practicable. Thus small hard particles were observed in an experimental lead cable alloy which were at first thought to consist of segregated impurities. Microanalysis showed these particles to be composed of iron and nickel, indicating that they had probably been accidentally introduced into the surface during the extrusion process. Paper removed from a condenser that had failed on test was found to contain microscopic particles of iron, iron rust, brass and carbonaceous aggregates which had also been accidentally incorporated during manufacture.

The isolation, detection and determination of traces of impurities or substances otherwise associated with large quantities of a given material have benefited through the application of microtechnique. Methods have been worked out for determining sulphur and phosphorus in steel and for silver in lead in which these impurities are all present in quantities less than 0.001 per cent. Acetic acid has been isolated from the corrosion products occurring when lead cable is exposed in creosoted wood ducts. The quantity actually present is usually very small, amounting to between 0.01 per cent and 0.001 per cent of the weight of the corrosion product.

Electrolytic corrosion in the windings of relays and other similar types of apparatus may occur as the result of minute quantities of salts present in the insulating materials or acquired from the manu-

facturing environment. These salts furnish electrolytes when the humidity is relatively high, dissolving the copper at certain poorly insulated points in the winding until the wire is eventually severed. In tracing the sources of this type of corrosion, microtechnique has afforded the only satisfactory method of attack.

Recently studies have been made to learn the effects of the dusts found in the telephone central office on the functioning of machine switching equipment. In these studies, microchemical methods have figured largely in the identification of the individual dust particles as well as in the quantitative determination of the major type of components.