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MICROCHEMISTRY IN RESEARCH AND INDUSTRY*

by

H. C. Harrison

Analytical chemistry is probably the most fundamental branch of chemistry. Before work involving inorganic, physical, organic, physiological or any other branch of chemistry can be carried on, it is essential that the composition of the materials used be known. The only way to obtain this information is by analysis, yet until about twenty years ago developments in analytical techniques and procedures had been woefully neglected. During the 75 preceding years, methods of qualitative and quantitative analysis had not kept up with advancements in other fields of science. During this period many of the basic instruments now widely used in analytical chemistry had been fairly well developed, yet little attempt had been made to apply them to analytical problems. It is true that research in this field is much less spectacular than that in many other branches of chemistry, and the general attitude appeared to be that analytical procedures had been worked out for the most common substances, and even though most of these methods were time-consuming this unfortunate feature was just something to be endured.

There is no authentic record of the development of the first balance, yet we know that a balance was used by Archimedes in 280 B.C. when he performed what was probably the first recorded quantitative experiment. In an attempt to discover whether air had weight, he placed an inflated bladder on the balance and then deflated the bladder. As he found no difference in weight after deflation, he concluded that air had no weight.

Janssen invented the first microscope in 1590. In 1678 Hooke published Micrographia, the first book on microscopy, yet the microscope did not take its place as an indispensable analytical tool until the early 1900's, and it is of interest to note that C. W. Mason, a graduate of the chemistry department of the University of Oregon, played an extremely important part in the development of modern chemical microscopy.

Newton performed his historic experiments on the nature of light in 1666 and in doing so actually developed the fundamentals of spectrochemical analysis. In 1758 Andreas Sigsmund Morggrof, a pioneer analytical chemist, showed that sodium and potassium could be distinguished in a flame. In the late 1700's and early 1800's discoveries were made which have proved to be of extreme importance in present day chemistry. Herschel discovered the infra-red region of the spectrum in 1800. Ritter discovered the ultra-violet region in 1801. Davy developed the method of electrolytic deposition in 1806. It was during this period that Berzelius, undoubtedly one of the greatest of all analytical chemists, was doing much of the research which proved to be the ground work for analytical chemistry up to the present time.

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* From a talk given by Dr. Harrison, chief chemist and spectroscopist of the Department of Geology and Mineral Industries, to the Department of Chemistry, University of Oregon, April 25, 1944.

Working in a laboratory set up in two ordinary rooms without furnaces, hoods, gas, or water, and with a sink consisting of a stone water-holder with a stopcock and a pot standing under it, this chemist analyzed more than two thousand chemical substances, and determined the atomic weight of fifty different elements with remarkable accuracy. The scheme of blowpipe analysis devised by Berzelius is very similar to the one in use at the present time, and a large number of his quantitative procedures form the basis of present day quantitative techniques.

In 1859 Bunsen and Kirchoff built the first modern spectroscope and with its aid discovered the elements rubidium and cesium. One of the types of spectroscopes in use at the present time is almost identical with the one built by Bunsen and Kirchoff. These two men studied the spectra of a number of elements and laid the groundwork for the science of spectrochemical analysis. By 1864 the knowledge of how to produce spectra of a number of metals was available, and the elements rubidium, cesium, indium, and thallium had been discovered with the aid of the spectroscope. However, the original expectation that this method of analysis would find widespread use did not materialize, and even today the majority of chemistry students are not instructed in chemical spectroscopy. There are a number of reasons why this method has been neglected, among which might be listed the fact that its extreme sensitivity frequently causes confusion in the mind of the inexperienced worker. The flame method of spectral excitation is limited in usefulness and it was not until arc and spark sources were developed that full advantage could be taken of the spectroscope. When the arc or spark was used many elements gave spectra which were very rich in lines and, until wavelength tables had been compiled, it was frequently easier to make a routine chemical analysis than to interpret the spectra. Widespread application of the spectrograph was retarded also until photography could be applied. Fifty years ago photography was not well developed and this is the only way of satisfactorily recording the ultraviolet region of the spectrum; it is in this portion of the spectrum that most spectrographic investigation is carried out. The science of spectroscopy did not progress to any extent after Bunsen's death until the medium size quartz spectrograph was developed in 1909 and the large quartz spectrograph was developed in 1912. The modern reflection grating spectrograph is a relatively recent development which was not made efficient until the method of sputtering or evaporating aluminum on glass had been developed. Previously reflection gratings were made of speculum metal and only a very small proportion of the light was reflected and made available for analysis with the result that sensitivity of the spectrographic method was very low. Today spectrochemical analysis is almost indispensable in the metallurgical industry and is widely used in many fields of chemistry.

In the early part of the 1900's, analytical chemistry began to emerge from the doldrums, and we are now in a period of intense interest in the development of analytical methods and instruments for doing analyses in hours or minutes, which previously had required days, weeks, and even months. The modern analytical chemist can no longer confine his activities to "wet work" using time-proved methods involving little more than weighing, precipitating, titrating, drying, and re-weighing. Instead he must be a combination of research chemist, expert machinist, radio technician, electrical engineer, and optical physicist. He must know something about emission and absorption of light, recording and non-recording mechanisms, and photography; he must have an understanding of vacuum tubes and amplifying systems and must be able to apply all of these diverse phases of knowledge to the repair, maintenance, and development of his apparatus.

During World War I when our supply of dyes from Germany was cut off, organic chemists in the United States were vitally interested in the synthesis of organic compounds, particularly those types which would replace or become substitutes for dyes. This type of development was extremely fortunate for analytical chemistry because, in determining the properties of these thousands of newly synthesized organic compounds, it was discovered that a number of them were specific reagents[1] for qualitative identification of ions, and

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[1] Specific reagent is a reagent which gives a characteristic reaction with one and only one ion.

in fact some of them were of sufficient value to indicate their use as new qualitative precipitating agents or as indicators in volumetric titrations. Organic reagents for qualitative analysis were not entirely new at this time as they had been used as indicators for determining pH values, and for some time dimethylglyoxime had been used for the determination of nickel.

A number of Austrian chemists, among whom should be listed Pregl, Emich, and Feigl, developed a field of chemistry which is very much in use at the present time. Pregl developed, mainly in the field of organic chemistry, a great number of methods of analysis whereby it is possible to make extremely accurate quantitative analyses using samples weighing from 3 to 5 milligrams (about one hundredth of the quantity used in macro[2], or large scale, analysis). Much of his apparatus consists of cleverly modified forms of similar macro-equipment and the use of this type of apparatus caught the fancy of many chemists. These Austrian chemists were working along the line of microchemistry[3] as early as 1918 - a time when there was intense activity along the lines of organic chemistry. As Professor of Analytical Chemistry at the University of Vienna, Dr. Fritz Feigl conceived a logical version of microtechnique whereby optical instruments were not required. His procedure involved the use of large-sized drops of solutions and this led to the terminology of "spot analysis" for his system. Feigl worked systematically in the whole field of analytical chemistry. He carried on extensive research programs and with the help of his students supplied the German chemical journals with information concerning Spot Tests by Feigl and his workers.

Feigl condensed all of his literature and personal experiences into a comprehensive book which was published in German in April 1931. In spite of its importance it did not receive proper recognition in this country until it was published in English in 1937 under the title of Spot Tests. The textbook Elementary Chemical Microscopy, written in 1914, was revised and published under the title of Handbooks of Chemical Microscopy by Chamot and Mason, and these books did much to awaken interest in the use of the microscope in chemical analysis and in the identification of a number of different kinds of substances such as hairs, fibers, different kinds of paper, etc.

With the advent of spot tests, chemical microscopy, organic microanalysis as taught by Pregl, the use of organic reagents as specifics, and the renewed interest in spectroscopy, analytical chemistry as a science received what is frequently referred to in the vernacular as a "shot in the arm." Chemists who had been accustomed to analytical methods handed down for almost fifty years were suddenly confronted with a maze of new chemical techniques, most of which had not undergone the test of time. In fact some extremely promising techniques such as Professor Heyrovsky's method of analysis using the polarized dropping-mercury-electrode were not given the immediate attention that they deserved.

Some of the confusion which occurred in the early and middle 1930's was undoubtedly due to the fact that enthusiasts for each of these new methods made extravagant claims, and it was only after each of the methods had been thoroughly tried out that it was learned that none of these methods would replace all other analytical methods. It was found that each had a definite value and when used to supplement each other they allowed the chemist to attack many problems which twenty-five years ago seemed insurmountable.

It is now agreed that procedures using microtechniques have their place along with macromethods. They have definite advantages over macromethods but they also have their limitations, and when these limitations are understood and taken into consideration it is frequently found that microtechniques will advantageously replace a number of techniques employing macromethods.

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2. Macroanalysis is performed on a relatively large scale as compared to microanalysis.

3. Microanalysis is performed on minute amounts of material usually requiring very sensitive or small-scale apparatus.

When we think of microanalysis our main thought concerns the advantage of being able to achieve the desired results with only a small quantity of sample, and in many instances this is the primary consideration in choosing a micromethod over a macromethod. However it is important to remember that the time element should also be taken into consideration in choosing a method. In industry, time is money and a chemist working for an industrial concern is usually under constant pressure to complete his analyses as rapidly as possible. Micromethods tend to employ a greater number of specific tests than do comparable macromethods, and this frequently means that numerous short cuts can be taken in most routine procedures. From the standpoint of the teacher, the consensus is that students are more keenly interested in those procedures which employ micromethods and apparatus. A group of students using micro- or semi-micromethods can be expected to complete more work in unit time and with more accurate results than a similar group using macromethods.

Unfortunately all micromethods are subject to a common error which might well lead to erroneous analytical results if the analyst does not take suitable precautions. This is often referred to as the sampling error. No analysis, no matter how carefully performed, should be reported to a greater degree of accuracy that that of the method used in obtaining the sample. The sampling error is a nightmare to all analytical chemists but is particularly serious whenever micromethods are used. Micromethods employ a much smaller sample than macromethods and therefore extreme care must be taken to be certain that the sample used in the analysis is truly representative of the bulk of the material being analyzed. There are a number of precautions that can be taken in obtaining a representative sample, but in many cases such precautions require so much time or trouble that it might be better to make the analysis using macroprocedures. In some instances, particularly when the microtechnique is being used on solutions, it is possible to put a large amount of material into solution and make the analysis on an aliquot portion. Each sampling problem should be carefully considered in the light of the method of analysis to be used if micromethods are to yield reliable results. Unfortunately the general public does not have an understanding of the sampling problem. The analyst frequently receives a piece of rock about the size of a robin's egg accompanied by a request that it be analyzed for certain elements. The analysis is made and it is later learned that the analytical results are taken as proving that the whole mountain from which the rock was taken has the identical composition as that of the rock submitted for analysis. Another problem frequently encountered by analysts is that of receiving a sample too small even for micromethods. It is not uncommon for someone to send in a fifty to one hundred pound sample for spectrographic analysis. This is not a serious problem as the sample can be split down and a truly representative sample obtained. If the sender comes to the laboratory to discuss the results of the analysis he frequently asks how much of the sample was used for analysis and, upon learning that about 100 mgs was used, he remembers how much it cost him to send the original sample and the next time he submits a sample which is too small to be truly representative or even too small to make check analyses. One spectrographic laboratory in the East has established the policy of requiring the sender to put small samples in the electrodes to be used in the analysis so that all of the responsibility for possible loss of the sample will be assumed by the sender.

Let us review rapidly some of the different branches of microchemistry and see if we can evaluate these methods with regard to their use in research and industry.

1. Micro-organic analysis as introduced by Pregl and later improved upon by numerous other workers: This type of analysis has proved to be indispensable to the research chemist working in the field of organic chemistry. It affords the only rapid method of obtaining an ultimate quantitative analysis of an organic compound, and also enables one to obtain the quantitative analysis of organic compounds for a large number of different organic radicals. In the field of synthesis of new organic compounds it is essential that the composition and a number of physical properties be determined before the identity of a new compound is established. There have been any number of instances in which an organic

chemist has spent a year or more synthesizing or isolating an organic compound, and the fruit of his labors consisted of not more than a few hundred milligrams of the organic compound. He usually must determine percentage of carbon and hydrogen, and in addition must know the melting point or boiling point, and the percentage of a number of other elements such as nitrogen, phosphorus, halogens, and sulfur. The size of his sample makes it imperative that micromethods be used. In routine organic analysis, semi-micromethods for organic combustion, nitrogen, and a number of other determinations are now widely used.

2. Chemical microscopy includes a number of different types of analytical procedures. Most of these procedures are qualitative in nature, and the majority of tests for anions and cations involve ionic reactions quite similar to those used in both micro and macro qualitative analysis. It is usually necessary to make a number of group separations and to detect the sought-for ion by means of a color reaction or by converting it into a crystal form which is characteristic and easily identifiable. Identifying tests have been established for nearly all of the known metals as well as most of the inorganic and some of the organic anions, and therefore it is much more versatile than most macro or micro qualitative procedures which usually include only about thirty odd cation identifications and a few anion identifications. In addition to routine qualitative ion determination, chemical microscopy has the great advantage of employing the optical properties of crystals as a means of identification, and by this means it is possible to differentiate between chemical compounds which have identical or nearly identical chemical composition yet differ greatly in optical properties.

Another type of microanalysis employing the microscope as the main tool is petrography. This type of analysis is of extreme importance in certain fields of science particularly in geology and mineralogy. The technique varies according to the type of work being done but in general petrographers who work on rocks and minerals prefer the thin-section technique while those working on industrial problems make more use of the oil-immersion method. In the thin-section method the material to be studied is cut in a thin slice and then ground on a special type of grinding wheel until the rock section is transparent to light. Using this technique the material under investigation is studied in about the same form as it originally existed, while if the powdered method is used the sample is crushed to a powder and thus the original structure is destroyed. Both types of technique have their place and a petrographer should be equally familiar with each. The main advantage of petrography seems to lie in the fact that the compounds in their original material can be identified and this is impossible when methods are used which require that the sample be put into solution to obtain ions, or when the physical character of the sample is altered. The main disadvantage of petrography is that opaque substances are not susceptible to this type of analysis except by using reflected light from the surface of polished sections and these techniques are not as well developed as in the thin-section and oil-immersion methods.

One of the outstanding spectroscopists, working in the field of rocks, ores, and minerals, has said that the real secret of his success rested in great part on the fact that he was working in the same laboratory with a good petrographer. Petrography and spectrography supplement each other in this type of work and whenever possible should be used jointly on an investigation.

3. X-ray analysis plays its own part as a valuable tool in the hands of the scientists. It is used in metal testing, as an important asset to research laboratories; it is almost essential in certain types of mineral identification, and in numerous other applications. Until a few years ago X-ray analysis was rather limited by the fact that very few tables of fundamental figures and patterns had been published. Each worker had to work out his own salvation and thus much fundamental work was repeated by a number of scientists. About 1936-1937 an extremely important list of these data was published in a special edition of the American Chemical Society, and this list has greatly stimulated

work in this field. It is to be expected that interest in X-ray methods will continue to grow, and it is safe to predict that within a relatively few years most universities will offer some type of course in this field.

4. The use of the electron microscope is a relatively recent development. In 1937 Dr. Louis Caryl Graton, a Harvard professor, announced a new microscope weighing about one ton, which with utmost precision, using a range of 6000 diameters, can spot units of gold so small that 40 billion of them would be worth only one cent. In June of 1938 German technicians announced perfection of a super-microscope using beams of electrons instead of waves of light, with a magnification factor of 20,400. Electron beams are straightened in a magnetic coil, passed through the specimen to be studied, focused in another coil; impressions are made on photographic emulsion; voltage used is 80,000. The magnification of this German instrument compares to that of ordinary high power microscopes about as the size of a penny compares to that of a pinhead. Instruments of this same general type were soon manufactured in this country by several industrial companies but the price was prohibitive for most universities or industrial concerns. A smaller sized model is now on the market for about $900. This price is very attractive but it may be that the same situation exists as was experienced in the field of spectroscopy when the market was flooded with small and medium sized spectroscopes. The purchaser often obtained one of these before he knew their real limitations, and frequently he was bitterly disappointed when the required work was just too complicated to be handled by a small instrument. There is little doubt that the electron microscope is a very powerful and useful tool in many fields of science but some of the claims at the present time might be classed as highly optimistic if not extravagant.

5. A very interesting but not fully recognized method of microanalysis particularly applicable to the study of ores and minerals is the contact print method introduced by Gregoire Gutzeit in March 1942. This is a combination of a number of methods in common use and includes the techniques of etching as used by the metallurgist, spot tests as used by the chemist, and micro-electroanalysis. It offers very interesting possibilities and will doubtless become used more often once it has become more widely known. The method is a modification of etching tests sometimes used in the identification of ores but offers an advantage over such tests. Both the etch and the contact print method are used when working with opaque ores and minerals. In the etch tests a polished section of the material to be studied is prepared and this surface is then treated with different chemical reagents to determine which of the constituents of the material are attacked by different reagents. Etch procedures are rather slow and are reliable only in the hands of an expert. Their greatest disadvantage is that the polished surface is destroyed with each test, thus making any further microscopic examination impossible without regrinding and repolishing. The new face being different from the first one, no localization of the elements is possible.

In the contact print method use is made of specific organic reagents which give colored complexes with one or more elements. The procedure used is as follows: "A piece of gelatin-coated paper is impregnated with a selective attacking reagent. It is then placed on top of the polished surface and pressed down in contact with the specimen. After the paper is removed it is developed in a reagent that is specific for the questionable ion. An inverted image of the position of the element on the polished surface thus results."[4] The paper may be either Eastman Kodak Co. "Kind 867" or a glossy photographic paper treated with thiosulphate and thoroughly washed in order to remove the silver salts.

This method has the advantage of giving a true picture of the localization of each element on the polished surface. It shows the presence or absence of a given element in each mineral particle by one test only, while by etch tests or microcrystalline tests

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[4] A.I.M.E. Mining Technology, T.P. 1457, p.2, March 1942

each mineral grain must be tested separately. Usually about ten prints can be made with one polish and it is easy to restore the original smoothness by rubbing the specimen on felt. In some instances electrolytic dissolution of the mineral is accomplished but this is limited to those minerals which are conductors of electricity. This is accomplished by connecting the mineral to the positive pole of a battery. The gelatin paper, soaked with an attacking reagent (an electrolyte), is pressed down on the polished surface by means of a metal foil which is connected to the negative pole of the battery. To prevent too rapid corrosion of the mineral the intensity of the electric current must be less than 50 milliamperes. Generally a potential from 2 to 6 volts is sufficient. Gutzeit's publication gives a large number of specific reagents and procedures; this article is recomcomended to scientists working in the field of mineralogy.

6. Analysis by means of the polarograph is rapidly taking its proper place in the field of chemical analysis. This type of analysis is based on the fact that various ions require different potentials for their discharge on a cathode. An electric cell containing a solution of the ions to be determined is subjected to a slowly increasing voltage and the current is plotted against the cathodic potential. When the potential reaches the discharge potential for a cation (positively charged ion) there will be an increase in the current at this point which will result in a sharp break in the plotted curve.

7. Spectrochemical Analysis. Like all other branches of analysis this technique has certain advantages over other types of analysis, but it has definite limitations.

As a means of making rapid and exhaustive qualitative analyses of all of the metals and a few of the non-metals it is unequalled. Using a spectrograph, one can make analyses in an hour which would take days, weeks, or even months by other methods; for example:

a. The qualitative and quantitative analysis of hafnium in the presence of zirconium.
b. The qualitative and quantitative analysis of rhenium in the presence of manganese.
c. The quantitative analysis of samples for small amounts of such elements as beryllium, tin, zirconium, gallium, rubidium, cesium, and lithium.
d. The detection and quantitative estimation of rubidium in the presence of excessive amounts of potassium or the detection and quantitative estimation of cesium in the presence of excessive amounts of sodium; and small amounts of strontium in the presence of barium and calcium.
e. It is the only completely satisfactory method for the analysis of the rare earths particularly when there are several of this group present in the same sample, this being the usual experience.

The limitations of this method are almost entirely in quantitative work. Quantitative determinations always have a limit of accuracy which usually runs around 10 percent error in routine analysis. For constituents which run 10 percent or more in a sample, some other type of analysis is usually better but, as the percentage of the desired constituent decreases in the sample, spectrographic analysis becomes more applicable and, at 0.1 percent and lower, it is usually more accurate than other quantitative methods. In routine analysis the time necessary to set up a procedure is an important matter. But in routine analysis on the same type of sample day after day the method is unexcelled both in accuracy and in time.

8. Fire Assay. This is probably the oldest known method of analysis. It is really a small scale method of smelting. Analysts in the western part of the United States are more familiar with this method than chemists in the East. It is the most satisfactory method for the analysis of ores for such metals as gold and silver and the platinum group of metals (platinum, palladium, ruthenium, rhodium, iridium, and osmium). When used in conjunction with spectrography, extremely small quantities of these metals can be detected and quantitatively determined.

At the present time there is no one method of analysis which might be termed a universal "cure-all." Each known method has its own particular field and each method has its limitations. By recognizing this fact and by using all of the methods applicable to any problem the analyst can go far toward getting the correct answer. This is an age of mechanization, and analytical chemistry is rapidly following the trend. A student of analytical chemistry who intends to continue with this field as his profession would do well to learn as much as possible about optics and electrical set-ups, which of course include amplifying systems, and to acquire at least a nodding acquaintance with some of the analytical methods used in fields outside of his own specialty. If he is well grounded in the principles of mathematics, physics, and chemistry, he has a foundation upon which to build when he is suddenly thrust into other fields of science, and it usually happens that a graduate seldom does all of his industrial work entirely within his own rather narrow specialty.

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HARRISON COMMISSIONED IN NAVY

Dr. H. C. Harrison, Chief Chemist in charge of the Department's spectrographic laboratory, has been commissioned lieutenant in the Navy and left on May 11 to engage in specialized work. Dr. Harrison, who received degrees from Washington and Lee and Cornell Universities, came to the Department in 1942 from the New York State College of Ceramics where he was professor of chemistry. He installed the Department's 3-meter grating spectrograph made by Baird Associates, and set up analytical techniques for the great variety of materials received for analysis. In addition to mineral and metal products, these materials included poisons, samples used as evidence in crime detection cases, and vegetation samples relating to agricultural research.

Miss Esther Miller, ceramic engineer and formerly assistant to Dr. Harrison, has taken over the spectrographic work of the Department.

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BLAST HOLE DIAMOND DRILLING

A particularly interesting and useful booklet for mining engineers has been issued by J. K. Smit & Sons, 157 Chambers St., New York, dealers in diamond drill bits. This illustrated booklet traces the development of diamond blast hole drilling and fully describes such applications at many of the large Canadian mines including Noranda, Aldermac, Waite Amulet, Flin Flon, Howe Sound, and Steep Rock Iron Mines. A discussion of drilling equipment is included. The publication is sent free of charge on request.

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