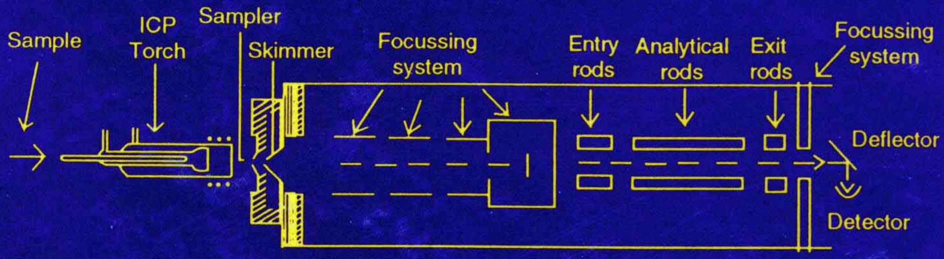

UNDERGRADUATE INSTRUMENTAL ANALYSIS

Fifth Edition,
Revised and Expanded

James W. Robinson

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Preface to the Fifth Edition

The field of analytical chemistry is expanding at an explosive rate. Automation and new instrumental techniques have increased scientific knowledge by leaps and bounds while greatly reducing operator error. The undivided attention to tedious details and the almost artistic skills needed to get accurate results are no longer a cornerstone of the field.

Within living memory, the determination of components at the 0.01% concentration level was a challenge, usually accomplished by taking a large sample and concentrating the analyte by any means possible "à la Madame Curie." Today, numerous analytical techniques need no sample preparation but are capable of detecting part per billion and part per trillion concentrations. In other advances, huge protein molecules can now be fragmented and characterized, and these techniques are providing the basis for cloning and gene modification. The information gained from these powerful new techniques can be invaluable in understanding chemistry but destructive when applied blindly to ethical or legal matters.

These days, analytical chemistry is concerned with applying a multitude of instruments to answer questions we did not even know how to ask until these very techniques revealed them to us. Such questions are: What are the health effects of various toxic materials at the part per million or part per billion levels of concentration? Why are they toxic? How can we prevent deleterious health effects? How do we analyze semiconductors for impurities when the impurities are at the 10^{-8} g/g level? How do we separate optically active drugs and investigate their different physiological effects?

All these everyday problems involve using complex equipment from HPLC to ICP–MS, and the analytical chemist should know the best procedure to use to solve the problem, the limitations of the methods, and other analytical techniques that will give corroborating information.

We have documented the basic chemistry and physics of these innovations and presented them in terms understandable to the chemist and the nonchemist alike. Also, we have provided examples of the applications and shortcomings of each technique and illustrated how to report the data so that the results are meaningful to all concerned.

Each chapter is written in sufficient depth to be used for an advanced-level instrumental analysis course. The range of techniques covered allows the instructor a wide choice of topics. For analytical chemistry at less advanced levels, the book can be used by chemists and nonchemists alike.

For courses such as organic chemistry lab, the fundamentals presented in Chapters 1–6, 13, and 15 are suggested. These chapters cover qualitative and quantitative molecular analysis. To this end, sections on interpretation of IR, NMR, and MS spectra have been added to the interpretation of UV spectra. Chapter 7–10 and 16 may be added for the traditional sophomore quantitative analytical course.

To help in understanding the subject matter and for out-of-classroom assignments, numerous problems (and answers in a solutions manual, which instructors may order from the publisher) have been added for each chapter.

Keeping pace with the advances in analytical chemistry is imperative for all scientists in order to operate at maximum efficiency and to stay abreast of current research in all scientific fields utilizing analytical chemistry. We hope this text serves this function for all such scientists.

James W. Robinson

Preface to the Fourth Edition

The book covers the more common instrumental methods used in analytical chemistry. It is written descriptively for a terminal course in analytical chemistry for the nonchemistry major and chemistry major alike.

It is not anticipated that the student will become an expert in any of the fields covered after reading this book. However, he or she should become familiar with the fundamentals of the methods, such as the bases of the techniques, the information provided, the difficulties involved in obtaining this information, and what information cannot be obtained from the various methods described. If all the techniques are understood, the student should be able to select the most useful analytical approach for characterizing typical samples. He or she should also be able to suggest alternative methods for confirmational purposes. The nonanalytical chemist should find this book helpful in deciding on the analytical methods to use to obtain the needed information and the methods' reliabilities.

The various spectroscopic methods are presented in order of decreasing wavelength of the radiation involved. Consequently, the first topic discussed in this field is nuclear magnetic resonance; the last topic is x-ray spectroscopy. A particular analytical course may not cover all the chapters presented, so each chapter has been made as self-explanatory as possible. It is not, therefore, necessary to read a major part of the book in order to understand any particular chapter. To achieve this goal some aspects of the presentation have been somewhat scattered and may seem repetitious; however, it was felt that the advantages of this approach far outweigh the disadvantages.

It was also felt that, in view of the many well-written and reliable books available on volumetric and gravimetric analysis, it would be superfluous to discuss these topics here. Consequently, no detailed discussion has been devoted to volumetric or gravimetric analysis or to qualitative analysis using chemical schemes. This is not to say that these methods are not important; they continue to have their place in analytical chemistry and will do so for many years.

James W. Robinson

What Is Analytical Chemistry?

Perhaps the most apt definition of analytical chemistry is "the qualitative and quantitative characterization of a material or materials." This broad definition includes many functions carried out by analytical chemists but does not differentiate these functions from those of many other scientists. But, an analytical chemist can be described as someone who publishes in analytical journals and attends analytical meetings.

One of the prime functions of the analytical chemist is the qualitative and quantitative determination of the elements present in chemical compounds. From these determinations an empirical formula can be derived for newly synthesized compounds, natural products derived from living tissue, newly developed drugs, new plastics, and so on.

Other functions of the analytical chemist include the elucidation of the molecular structure of compounds such as proteins, the determination of the distribution of isomers in a mixture, and the determination of impurities in products as diverse as drinking water, motor oil, sea water, cigarette smoke, steel, blood, and plants. An important issue today is the effect of impurities in our environment. Are some of them toxic or carcinogenic? Analytical chemistry plays a major role in determining these effects by establishing the quality and quantity of trace materials present in foodstuffs, toxins, pollutants, drugs, cosmetics, and so on.

Physical properties must sometimes be measured. For example, crystallinity has a profound effect on the strength of polymers. A manufacturer must know if a polymer will tear when it is being used (it must tear easily if it is the wrapping on a package of cigarettes, but it must not tear if it is the protective wrapping on a scientific instrument). It may also be necessary to determine how long it will take a polymer to decompose if it is left out in the sun or rain. If it is to be used for roofing, we want it to last forever; if it is to be used as a garbage bag and then thrown away, we want it to decompose—otherwise it will become a problem in solid waste disposal. The same questions may be raised about varnishes and paints. Usually, these are the questions that must be answered by the analytical chemist.

Another problem tackled by the analytical chemist is the determination of the molecular weights of various compounds. A single compound does not present a very difficult problem, because it has only one molecular weight, but a mixture of compounds will encompass a whole range of molecular weights. This is particularly true with polymers and naturally occurring products, such as those found in plant and animal life, and it is then necessary to determine the molecular weight range and distribution of the compounds present.

The analytical chemist is also called upon to determine the compositions of mixtures. If two or three components are present in a mixture, it is often important to know how much of each is present. This information is necessary to such people as metallurgists and engineers who prepare alloys and need to know the actual composition of the alloys they have formed.

Companies that manufacture soaps or detergents need to know how much of their product is biodegradable. Federal law requires that all detergents and soaps be biodegradable. When soaps used in the household or laundry are washed down the drain and into our rivers, they must not persist as soap. Bacteria should be able to attack the soap and degrade it into other forms of matter. If the soap cannot be degraded, it will create foaming problems in rivers and streams; contamination of drinking water is possible, and under severe conditions the fish and vegetation in these rivers will be killed. The analytical chemist can determine how fast a detergent will be degraded in rivers or sewage.

In medicine, we are beginning to understand the effects of trace metals on the different parts of the body, and we are now trying to correlate the presence or absence of these metals with the occurrence of certain diseases. The analytical chemist in medical research is asked to provide methods of identifying and determining these trace metals.

For many years, analytical chemists were concerned with the chemical properties of the materials analyzed. It was common practice to dissolve the sample and then carry out some chemical reaction on the chemical component of interest. The extent of the reaction was then measured, and the concentration of the chemical component present in the sample was calculated. This system served analytical chemists well in the past. Schemes of qualitative and quantitative analysis were developed based on chemical reactions. Such schemes were valuable both to teach reaction chemistry and to carry out qualitative and quantitative analysis. The most important analytical fields involved were volumetric and gravimetric analysis. Unfortunately, these procedures demanded a high degree of skill and loving care on the part of the analytical chemist to produce reliable results. The analytical chemist who worked successfully in these fields was an artist. Care and patience were of prime importance in getting correct results every time an analysis was run.

Because modern industry has grown so quickly and the continuous control of manufactured products has become such an important and vast problem, the few skilled analytical wet chemists cannot provide the information needed. Masses of data are demanded every day by people in many walks of life. In hospitals, diagnosis of illness is dependent to a large degree on the routine determination of sodium, potassium, calcium, and magnesium in blood. In industry, many stages of manufacturing require quality control by analysis to make consistently good products. In this competitive world, we cannot afford to make substandard products.

Analytical chemists are also called upon to distinguish between master artworks and fakes. In the process of carrying out their examinations, they must not destroy or blemish the work of art. The methods used must be *nondestructive*, a factor that has become increasingly important to many areas of analytical chemistry in recent years.

Hiring more people to carry out analyses based on chemical reactions is not the answer. Frequently the newly hired analytical chemist has neither the interest nor the skill to perform like the artists of old. Furthermore, the time involved in running volumetric and gravimetric analyses is very long, and industry cannot afford to delay decisions until the analytical chemist can obtain his or her results.

As a response to these demands analytical chemists have had to turn to new ways by which to carry out analyses. These methods are generally based on the physical properties of the material. Extensive studies are being made on measuring and understanding the interactions of radiation and matter. By measuring the radiation effects, we are able to determine not only what is present in the sample, but also how much. Based on these interactions, instrumentation has been developed to carry out analyses on a rapid and even continuous basis.

A large number of important fields of physics and chemistry have been united to provide the answers required by analytical chemists. The procedures developed range in complexity. Some methods are completely automatic and require very little attention from an operator; on the other hand, some instruments have been developed that require a high degree of skill to operate. Furthermore, some equipment provides results that take years of training to interpret; however, the information obtained by using this equipment cannot be obtained by other methods.

What is the function of the analytical chemist? The first requirement is to provide data to other scientists. These scientists include other chemists, biochemists, biologists, physicians and medical technicians, agricultural scientists, metallurgists, engineers, health scientists, nutrition scientists, and environmentalists, among many others. To satisfy them, the analytical chemist must be cognizant of all the analytical methods presently available. When asked to characterize a sample, he or she should know what analytical procedure can be used to best advantage to obtain the information.

What can other scientists gain from analytical chemistry? In order to make optimal use of the techniques that have been developed in analytical chemistry, other scientists should know what information is available to them through analytical chemistry and, almost as important, what is not available to them. If scientists understand the principles of the various fields of analytical chemistry, they will know if they can obtain the information they desire, and they will also know the best way to obtain it; otherwise they may waste much time trying to get the information by some indirect means. Knowledge of analytical chemistry is highly desirable in all people who use analytical data to arrive at a decision in their work.

Scientists seeking information from analytical chemists must provide reliable samples that will give accurate results when analyzed. They should also communicate as much information concerning the samples as possible before the analytical chemist starts to work. This enables the analytical chemist to make the right choice in selecting a technique to solve the problem at hand.

Research analytical chemists have somewhat different functions. They should be aware of and contribute to new developments in chemistry and physics. Their most important role is to harness these developments for analytical chemistry so as to provide either sources of new information or more rapid and more sensitive methods of obtaining information.

ALL THOSE "ILLIONS"

Nowadays, determinations of concentrations at the part per million, part per billion, and part per trillion levels are commonplace. The mind has difficulty distinguishing these different ''illions'' and boggles at trying to grasp their meaning. One way to do this is as follows:

A million seconds is about 12 days (actually 11.57). So a *part per million* (ppm) is as significant as 1 second in 12 days. Similarly, a billion seconds is 32 years (actually 31.7). So a *part per billion* is as significant as 1 second in about 32 years. Similarly, a trillion seconds is 32,000 years. So, a *part per trillion* is as significant as 1 second in 32,000 years.

Christ was born 2,000 years ago, the earliest recorded human history was 5,000 years ago, the last ice age was 17,000 years ago. Does that help to get these ''illions'' into perspective?*

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*It is interesting to note that the national debt is $4 trillion. If we paid $240,000 per minute, paying no interest on the principal, it would take 32 years to pay it off.

Numerous analytical techniques are capable of detecting part per billion and part per trillion concentrations. Some, like GC–electron capture, atomic absorption spectroscopy, and ICP–MS can operate at 10^{-14} concentration levels. This information can be useful in understanding body chemistry or can be destructive when blindly applied to legal matters.

Clearly, analytical chemistry is capable of answering questions we didn't even know to ask a few years ago. It is opening up new fields of endeavor at a prodigious rate. Keeping pace with the advances in analytical chemistry is imperative for all chemists in order to operate at maximum efficiency and to stay abreast of current research in all related fields.

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