

# THE BEGINNING COURSE IN QUANTITATIVE ANALYSIS\*

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The great importance of chemical analysis is widely recognized in industry. Whenever variation in composition affects the properties of materials, they are bought, made, used, and sold on the basis of tests and analyses. Likewise heavily dependent upon analysis are clinical diagnosis, enforcement of various laws, most chemical research, and many other activities.

From the days of Berzelius and Liebig, analytical chemistry has had a prominent place in the education of chemists. Continued recognition of this status is shown by the requirement of two semesters of work in the subject by the committee of the American Chemical Society which accredits colleges offering a major in chemistry. Probably every college of significance has at least one course in analytical chemistry.

If the subject is so well established, why should one reconsider the beginning course? Perhaps the most important reason is the ever-increasing number of new techniques and methods being published. Examination of current issues of *Chemical Abstracts* will reveal an amazing number of publications on new instruments and methods of analysis, and on improvements of old methods and instruments or adaptation of them to new situations. Many annual or biennial review papers summarize the progress in specific areas.

As a background for all of these advances we have a wealth of analytical information accumulated during the past two centuries. To introduce the student to the essence of all of this, the old and the new, what should be done and how may one do it? Judging by the many textbooks published, there are many different answers. Apparently all possibilities have not yet been exhausted, for new books continue to appear.

The present discussion is limited to quantitative analysis. However, the indispensability of qualitative analysis in a vast number of situations must not be forgotten. Experienced quantitative analysts know that in most situations it is very hazardous to try to apply a quantitative method to a material whose qualitative composition is unknown. The presence of unsuspected constituents may cause very erroneous quantitative data.

In considering the beginning course in quantitative analysis I presume to state again only my own views. Although they have been recorded, both in papers and books, it is frequently worthwhile to reconsider one's position. That others have different views is evident from many publications on the subject.

The definition of chemical analysis used is that attributed to Robert Boyle; namely, the determination of the composition of substances. It should be noted that this definition implies no limitation on the kind of techniques which may be employed.

## OBJECTIVES

Before deciding upon the content of a course, and on the method of administering it, one should be reasonably clear on the objective(s) of a course. Quantitative chemical analysis is no exception.

I believe that the over-all objective is to introduce the student to the body of knowledge generally considered to constitute quantitative analysis. More specifically, this means to sample the subject by selecting representative methods

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which will give a balanced perspective of the most important problems of analysis and of some of the methods of meeting them.

Probably few teachers actually try to train analysts as such, that is, to do particular determinations expertly. Only practice (correctly done) makes perfect, and this takes too much time for each new assignment. Rather, the objective is to impart a feeling for analysis, the basis of methods, how they are applied, the kind of data they yield, and something of the problem of obtaining reliable results. Not unimportant are the following psychological and educational by-products suggested many years ago by W. S. Frost: (1) stimulation of logical mental processes; (2) training of the memory; (3) practice in learning to work effectively; (4) cultivation of self-reliance and resourcefulness; (5) development of neatness and care; (6) education in dependability and integrity; (7) encouragement in the use of the scientific method; and (8) development of respect for natural laws.

#### BASIC OUTLINE

In theory at least, quantitative analysis encompasses the possible determination of all of the chemical elements, the many radicals and ions, and the almost numberless compounds. The last category alone comprises more than 600,000 organic compounds. At least one, and usually several, of these entities will be found in every separate natural and synthetic substance known. Thus, it should be evident that the analytical problems faced by the chemist are substantially limitless in dealing with all possible kinds of combinations.

Into what broad outline can one fit the basic operations and processes available to the analyst for determining desired constituents, in any possible relative amounts, in any and all kinds of substances, whether inorganic or organic? More than two decades ago I suggested considering the problem in terms of the unit operations and processes involved. The following brief outline is my best answer thus far.

I. *The sample.*—It seems obvious that analyses cannot be made without samples. The topics enumerated are most likely to be of concern in practical analysis.

1. *Selection and preparation.*—Homogeneous materials present no problem, provided enough is available for the required determination(s). In contrast, obtaining a representative sample from some heterogeneous materials is one of the most difficult analytical operations. In spite of this fact, a recent survey of 50 books revealed that 20% of them did not mention sampling.

2. *Measurement.*—Usually the amount of a desired constituent is reported in terms of the amount of the sample used. Percentage is the most common basis, although others are employed. Sometimes, as in densimetry, measurement is not employed, but it was necessary in establishing some kind of scale or calibration curve. The two most used methods of measurement follow.

a. *By mass.*—The operation of determining mass by weighing is known to every chemist. The equal-arm (analytical) balance is the analyst's best known instrument, a fact some instrumentalists forget. Solids, liquids, and gases may be weighed, although gases usually are not.

b. *By volume.*—Volumetric measurement is often used for liquids, and widely employed for gases. Unless otherwise specified, the liter, rather than the cubic meter, is the unit.

c. *Other methods.*—Occasionally some other method is used, such as manometry for gases.

3. *Preliminary treatment.*—Many kinds of samples require one or more preparative processes prior to measurement of desired constituents, even though no separation is necessary. The following types are most common: fusion; dissolution; and adjustment of conditions, such as acidity, oxidation state, and complexation.

II. *The desired constituent(s)*.—A quantitative analysis always involves the determination of one or more desired constituents. Unless there is some interference, one proceeds directly to such determination(s) on the sample after appropriate preliminary treatment(s) (if necessary).

1. *Separation*.—In case of interferences (known from qualitative analysis), separation is necessary unless provision can be made to correct for or avoid them. The following separative processes are widely employed: volatilization, precipitation, electrodeposition, dissolution, absorption, adsorption, ion exchange, and liquid-liquid extraction. There are others, of course.

It should be emphasized that such separations are always avoided, if possible. Except for any necessary preliminary treatment(s), here one finds practically all of the chemistry involved in a method of analysis. The objective, of course, is to isolate some system the purity of which is known with a certainty adequate to enable one to measure the desired constituent(s) with the required accuracy, or which is free of possible interfering constituents.

The necessary preparative chemical steps may be long, tedious, and exacting. Not frequently much experience and skill are needed to accomplish them. Sloppy manipulation and disregard of operative details may lead to serious errors. No separation process has any inherent connection with any particular kind of measurement.

2. *Measurement*.—In the determination of any desired constituent, by any kind of method, measurement is the final and inevitable analytical operation. Measurement consists, of course, in determining the number of times the standard goes into the unknown. The entity measured is always some property. It may be a specific property of the desired constituent, or of something bearing a known relationship to this constituent. Thus, to determine silver one may measure the mass of electrodeposited metal or of precipitated silver chloride. Or it may be a systemic property such as the density of a solution of sulfuric acid, from which the amount of desired constituent can be ascertained. No matter what the property, or the means employed to measure it, the operation is physics.

The number of properties measurable for analytical purposes is fairly large. The number of ways of measuring them is much larger. Altogether, the possibilities are bewildering to anyone except a widely experienced analyst. Thus, 72 kinds of spectrophotometers have been suggested. The field has developed until a monograph of hundreds of pages is required for each of a number of these techniques, examples being emission spectrometry, polarography, and titrimetry.

#### SELECTION OF MATERIAL

It is hoped that enough has been stated to indicate the enormous range of information available which deals with quantitative chemical analysis. It comprises (1) all of the chemistry—inorganic, organic, and physical—which is used to prepare systems for measurement, and (2) all of the physics basic to the instruments used to make the measurements. All measurement is instrumental.

What should the instructor select from all of this for a beginning course? Several items need to be considered.

*Nature of course*.—An important point is the kind of course. If it is for one semester, less material can be included than in one covering two semesters.

To enhance motivation, the student's interests may be considered. Thus, a one-semester course for students in home economics may well be slanted differently from one for students in chemical engineering. However, the principle of weighing a sample is the same in the two cases; but the girls feel better if their samples are baking powder, and the boys if theirs are soda ash.

*Emphasis sought*.—The course should be analytically realistic. That is, in the limited time available, it is probably a waste of time in most instances to dwell on abstruse theories of chemistry or physics. Also it is probably of questionable

value merely to press the switches and read the meters of a large number of instruments.

What seems much more desirable is a broad understanding of the problems and methods of analysis. This involves (1) the chemistry necessary, if there is any, to render the desired constituent measurable; and (2) the properties measurable, together with the means available and their limitations.

In addition, it has been my experience that the design of a workable method for a specified, new situation is a very enlightening exercise. Primarily it must be based upon information from the library. If feasible, it should be tried in the laboratory. This is a very simple introduction to research.

*Personal choices.*—Somewhat arbitrarily I devote the first semester to titrimetry and photometry, with some attention to the sample, particularly its selection, measurement, and preliminary treatment. Then in the second semester I cover gravimetry and polycomponent analysis, including the design of a method for a four-component hypothetical alloy.

Thus, this includes three very widely used methods of measurement. Using polycomponent samples in the second semester, such as limestone, bronzes, and alloy steels, provides a very practical situation for discussing the chemistry and techniques of a variety of separatory processes. Also, as time permits, the principles and applicability to these materials of other methods of measurement are discussed. A good example is the possibility of using emission spectrometry and electrometry for such materials

#### THEORY

Although one is accused occasionally of training determinators, rather than analytical scientists, it is doubtful if any instructor seriously attempts to achieve the former objective. Industrial laboratories do not train routine analytical operators as students are handled in college classrooms.

My advocacy of a broadly based viewpoint in teaching quantitative analysis contemplates the inclusion of some theory, both with respect to the chemistry and the physics involved. Generally the more basic the knowledge one has on a subject, the better.

The common meaning of theory is an interpretation or explanation of a phenomenon. That is, it concerns the how and why of things. For example, sodium chloride crystals are white and cubic; silver chloride is curdy, barium sulfate is crystalline, and hydrous ferric oxide is gelatinous; silver chloride adsorbs very little and barium sulfate strongly; and ferric ion forms with chloride ion yellowish  $\text{FeCl}_4^-$  and with fluoride ion colorless  $\text{FeF}_6^{3-}$  ions. Why are the stated facts true and how do the processes involved operate? Relevant theories are attempts to interpret such facts, as science consists of facts and their interpretations. Interpretation is the role of physical chemistry.

What should and can be done here is the most serious question in teaching quantitative analysis. Probably no two teachers would agree.

Firstly, what can be done? The great majority of students reach the course today as sophomores. Consequently, they are probably just taking calculus, and may be in their first course in physics. Most of them know little or no organic chemistry, and they have not taken physical chemistry.

Secondly, what is worth doing? Should the instructor attempt to go into the mathematical theory of sampling heterogeneous materials? When the sample is to be weighed, should he consider the theories of gravitation, of the engineering design of the balance, and of the corrosion of the weights? Assuming that the sample is a silicate and that the iron is to be determined absorptometrically as the 2,2'-bipyridine complex, should one take up the theories of the fusion process, the precipitation separation of the iron as the hydrous oxide, the reduction by hydroxylamine, the indicator action in adjusting the pH, and the complexation with the

2,2'-bipyridine? Then follows the measurement. Referring only to the detectors in absorptimeters, what theory is to be included for visual, photographic, and photoelectric detection?

I do not know the answers to these and many similar questions. Inasmuch as capable graduates come with a great variety of backgrounds, evidently no one viewpoint is critical in teaching. No doubt we should do what is feasible in the situation, but without forgetting that quantitative analysis is essentially a practical subject. Someone stated that quantitative analysis is half an art and half a science. Any relevant theory relates to the chemistry and physics involved in specific applications.

#### LABORATORY WORK

A course without laboratory work is comparable to a lecture or recitation course, or both, on driving an automobile without actually driving one. I have suggested certain objectives for a broadly based course. Part of these, especially the skill in, and understanding of, the art, can probably be achieved only in the laboratory. The science involved is a subject for the classroom.

What is selected is not critical as long as one achieves his basic objectives. The principles of weighing and handling a stable sample have nothing to do with the composition of the sample; as industrial materials, nonferrous alloys, alloy steels, and limestone do not go out of style because of current interest in plastics and uranium. In any case, the samples should serve as means for illustrating principles of chemical preparation and/or separation and of measurement, rather than as analytical ends in themselves.

Today it seems impossible to introduce students in any significant way to all of the apparatus and instruments available for separation and measurement. Anyway, I know of no evidence that industry wants the product of a button-pushing, meter-reading excursion past an array of expensive instruments.

Neatness, care, reliability, and an understanding of the basic problems of separation and measurement are desirable. Equipped with these, along with general intellectual capacity, a will to work, and ability to work with others, the student need not fear for his analytical future.

Unless measurement alone is the objective of a course, the samples should be realistic. The industrial analyst's first concern is always with materials. Thus, the titration of a solution of ferrous ion with permanganate illustrates nothing of the separative and preparative chemistry necessary if iron is to be determined in many kinds of materials. Practically, one seldom finds iron ready to be titrated. For large classes I believe in using a large series of analyzed samples, although for statistical evaluation, all students should use the same sample material for any given assignment.

Finally, the laboratory notebook should be mentioned. The instructor can do much here to cultivate sound habits of handling laboratory data. The particular form of book is not important, but the entries should be in a consistent form.

Specific entries should be adequate to enable one skilled in the art, i.e., one trained in analytical chemistry, to know the kind of sample, the method employed, and the supporting data for the results reported.

In addition, the record should be dated and signed by the determinator. These two items are musts if the record is to be submitted in legal cases, such as suits involving patents or law enforcement. Also in chemical companies often someone wants to know who did certain analyses long after the work was done.

#### NUMERICAL PROBLEMS

Two kinds of numerical problems interest the student and practicing analyst. One is predominantly theoretical in nature, and the other is even more predominantly practical in nature.

The first type of problem is essentially the application of simple physical chemistry to the systems being studied. Familiar topics involving ionic equilibria are solubility, solubility product, common and diverse ion effects, ionization, dissociation, pH, buffers, hydrolysis, complexation, instability, oxidation-reduction, and others. Such problems have long been considered basic in the more comprehensive texts on inorganic qualitative analysis. The subjects are equally important, of course, in quantitative analysis. The problems are largely theoretical.

The second type of problem deals primarily with the calculations which usually have to be made in the course of performing analyses. For example, direct-reading samples are weighed, vessels calibrated, titrants standardized, and amounts of desired constituents calculated. To be able to calculate the pH of a buffer system, the equivalence point of a given titration system, the instability constant of a complex, or the potential of an electrode in a given system, is very desirable; but to be able to make the calculations necessary for an analysis is indispensable if the results are to be useful. These problems are entirely practical in nature.

Incidentally, orientation tests of incoming graduate students have revealed that many such students are very deficient in solving the practical problems. One wonders if these individuals ever did any laboratory calculations.

Many years of teaching have convinced me that there is a very good correlation between the ability of a student to work numerical analytical problems and his understanding of quantitative analysis. Consequently, I have long made such problems a major part of my testing program.

#### THE TEACHER

The general outlook and training of the teacher have much to do with the success of courses in quantitative analysis. The blind cannot lead the blind, the ignorant cannot impart knowledge, nor can the uninterested generate interest. Often the teacher is one who majored and works in another area, but he was assigned the "quant" course because of necessity. He may never have done any real analyses of polycomponent systems, and probably he is unfamiliar with what is being done in industry. Out of this lack of background he states that gravimetric methods are passe, that burning carbon out of alloy steels at 1200°C is a "wet" method, and that we have only gravimetric, volumetric, and special methods of measurement. Or he writes that all samples must be dried, ground, and dissolved, although any experience with flue gas, water, and urine would have shown him that one does none of these operations with such materials.

There is considerable evidence that such deficiencies are too general for comfort. Perhaps the most serious need for beginning courses in quantitative analysis is for teachers who have analytical experience and knowledge, and who have a genuine sympathy for and interest in the subject.

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