

# THE USE OF QUANTITATIVE AND QUALITATIVE ANALYSIS IN THE GENERAL CHEMISTRY LABORATORY<sup>1,2</sup>

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The work of the freshman year at the California Institute of Technology is uniform—students taking basic courses in mathematics, physics, chemistry, English, and history. At the end of this year students preregister for the sophomore year and for the first time must select a professional option which consists of a sequence of courses leading to a degree in one of the fields of science or engineering. Since the end of World War II, there has been a continued decrease both in the number and in the average quality of the students electing at this time to enter the options in chemistry and applied chemistry. Even after taking into consideration the present glamour of physics and electronics, this decrease has appeared to be abnormally large. In fact there seemed evidence that the laboratory work of the freshman chemistry course was neither attracting the interest of the students in general, nor holding the interest of those who had been previously attracted to this field. In seeking an explanation of this situation three somewhat related questions emerged.

First, to what extent was the conventional laboratory work of the general chemistry course still unduly influenced by the period when chemistry was predominantly a descriptive science?

Secondly, since substantially all of the freshman students at the Institute have had high school chemistry of some type, to what extent was the laboratory work repetitive of this work and therefore lacking in providing either stimulation or evidence of progress.

Thirdly, to what extent was this laboratory work failing to recognize that both science and engineering are becoming progressively more quantitative in both theory and practice?

It is true that there had been an attempt to introduce more quantitative experiments into the freshman laboratory work. Experiments making use of Mohr burets and analytical type balances with a sensitivity of approximately one milligram had been introduced into the work, but there was little evidence that these experiments had proved to be particularly effective in increasing the interest in the work. In fact the introduction of this pseudo type quantitative work in the freshman year caused the work of the quantitative course in the sophomore year to seem frustratingly repetitious and monotonous, and the necessity of correcting some of the habits formed in the previous year intensified this feeling.

As a result of these considerations a committee from the Division of Chemistry and Chemical Engineering, composed of John Roberts, Carl Niemann and the author, was asked to consider a revision of the work of the freshman year and, if it appeared appropriate, of the entire undergraduate chemistry curriculum.

After considerable discussion, within the Committee and with other members of the faculty, this committee recommended that an experimental program be initiated in which the conventional laboratory work of the first two quarters of the freshman course was to be replaced by selected quantitative experiments

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<sup>1</sup>A report on the revised curriculum at the California Institute was given at the Symposium on New Ideas on the Four-Year Curriculum during the September, 1957 meeting of the American Chemical Society in New York City. This report was published in the *Journal of Chemical Education*, 35, 248 (1958). The author is indebted to Dr. William F. Kieffer, editor of that journal, for his generous permission to make extensive use here of material from that report.

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essentially the same as those which had been given previously in the sophomore course in quantitative analysis. This recommendation was based upon several assumptions and the committee was uncomfortably aware that the validity of these assumptions could only be demonstrated by resorting to the experimental method.

The first of these assumptions was based on the belief that at the present time freshman students, especially those with an interest in science or engineering and with the motivation to have taken a preparatory course in chemistry, were sufficiently mature to be more interested and challenged by quantitative laboratory work done on a professional level than by such work when it was reduced to the status of a pedagogical device. Also, it was believed that such students would be challenged by the opportunity of checking their own technical competence and achievements against professional standards and against the achievements of their fellow students.

The second assumption was based upon the belief that it would *not* be significantly more difficult to teach such freshman students quantitative techniques than it had been to teach these techniques to sophomores. In fact, it was believed that these techniques would be more interesting and challenging when they had not been preceded by similar work of a lower caliber. In addition, it was believed that these techniques could be so taught that they would illustrate the principles involved, not only in making quantitative analyses, but in making quantitative measurements with other instruments and in other fields of science and engineering.

Thirdly, it was believed that by a proper selection of experiments *the general principles of chemical reactions could be illustrated as effectively by such quantitative experiments as by the more descriptive and qualitative experiments generally used.* Finally, it was believed that the actual analysis of unknowns would prove more interesting and challenging to the student than would, for example, the determination of an equivalent weight which, as expressed by one student, ". . . had been determined fifty years ago fifty times more accurately."

The committee was aware that in general the quantitative analysis laboratory has not been noted for attracting students into chemistry. It was realized that the success of the course would be quite dependent upon the work being so oriented as to convince students, especially those without an initial interest in chemistry, that the objective of the course was not to train him to make analyses, but rather to give him some appreciation of the methods and the problems involved in making quantitative physical measurements regardless of the instrument used or whether these measurements were to be applied to chemical, physical, or engineering purposes. Also, he should be made to realize the value of this work in enabling him to develop a feeling for sources of error and for critically evaluating the validity of experimental data, regardless of its source. Above all, he should develop a respect for the experimental method and a realization that the experimental method is the basis of scientific progress. In recent years there seems to be an increasing tendency by students, both graduate and undergraduate, to avoid the experimental method. And this tendency seems to be accompanied by, or may result from, an inability to plan or execute experiments, to make pertinent observations, or to interpret those which are made. A further consideration leading to the recommendation to undertake this experiment was the fact that such an integration of the general chemistry and the quantitative analysis laboratory would achieve a substantial acceleration in the basic training of the student and thus would give him much more time in his junior and senior years, especially the latter, for undergraduate research or for more advanced courses in his field of special interests.

The freshman chemistry course at the Institute consists of two one hour lectures per week, given to the entire class of approximately 180 students; a one hour quiz period which is given to sections of approximately 20 students; and

two three hour laboratory periods per week. The lectures are given by senior staff members. During the first two quarters of the 1956-57 academic year one of the weekly lectures was usually given by Professor Pauling and was related to the material in his text, *General Chemistry*. The other lecture was given by Professor Harold Johnston and was related to the general principles, not the specific details, of the laboratory work.

This division of the lecture material was unfortunate, and this year all of the lectures of the first quarter were related to the laboratory work. They began with weight relationships, stoichiometry, units of quantity and of concentration, and then were directed towards the examples of chemical equilibrium involved in the laboratory work.

The so called quiz hour was in charge of the graduate teaching assistant responsible for the laboratory work of the section. The quiz period was used not only for quizzes but also for presenting and discussing the laboratory work in more detail and for answering questions related to either the lectures or the laboratory work. For want of a manual designed for this particular course, use has been made of elementary quantitative texts, freely supplemented by mimeographed material.

The laboratory work during the 1956-57 year began with use of the analytical balance and included methods for determining rest points, determinations of sensitivity with various loads, and a calibration procedure for weights from 1 to 5 gm. The student was then given calibration values for the entire set and he weighed an unknown object. This was followed by a conventional gravimetric determination of the chloride in a solid unknown; the silver chloride precipitate was weighed on either a sintered glass or a porous porcelian crucible.

Volumetric work was then begun and the student calibrated a buret at the 20 and 30 ml intervals. These weight and calibration procedures were not done as mere manipulative training but as a necessary means of establishing both the personal and instrumental capabilities and limitations involved in making a quantitative measurement. The corrections for air buoyancy and for temperature effects also illustrated the necessity for considering external variables. The students showed a surprising amount of interest in these calibration procedures. A standard silver nitrate solution was prepared by weighing the dried salt, dissolving it, and diluting it to volume. Following this a volumetric determination of the chloride in an unknown was made with chromate being used as the indicator. A potassium thiocyanate solution was then prepared and standardized against the standard silver nitrate; ferric nitrate was used as indicator. The thiocyanate solution was then used to determine the silver in an alloy or the mercury in an unknown solution. The final determination of the work of the first quarter was the identification of one of a series of compounds by means of the determination of the molecular weight by means of freezing point depression measurements.

In the second quarter the principles of oxidation-reduction reactions were illustrated by the preparation and standardization of a tri-iodide solution and its use for the determination of the antimony in a stibnite type ore. A thiosulfate solution was prepared and standardized and then used for the determination of the copper in an alloy.

Acid-base equilibria were then taken up and the laboratory work involved the preparation of hydrochloric acid and carbonate free sodium hydroxide solutions and a determination of their volumetric ratios. The sodium hydroxide was standardized against potassium acid phthalate. Determinations were then made of the concentration of acetic acid (vinegar) solutions and of the total alkalinity of various carbonate mixtures. At the end of this first year there was justifiable criticism of the preponderance of volumetric methods. Consequently, this year procedures involving colorimetric and simple constant current coulometric methods were introduced, along with the use of pH meters.

The laboratory work of the third quarter was shifted from quantitative measurements to qualitative analysis. This was done in order to exploit the unique potentialities of a system of qualitative analysis as a pedagogical device for teaching descriptive inorganic chemistry and the principles underlying chemical reactions. Because the pedagogical effectiveness of a system of qualitative analysis will be determined largely by the extent to which the major separations can be correlated with the fundamental properties of the elements and therefore with the Periodic Table, the system which was used was a simplified version of the one described by Swift and Niemann in *Analytical Chemistry*, 26, 538, 1954. This system was developed at the Institute for use by the Chemical Corps during World War II and the initial step consisted of a fusion with sodium peroxide and sucrose in a Parr bomb. Upon treatment with water a residue remained consisting of those elements forming oxides which were sufficiently insoluble and basic in character to remain as a precipitate in the strongly alkaline solution. This residue was separated and termed the Basic Element Group. The solution was divided into two portions. One portion was analyzed for those elements forming predominantly amphoteric oxides; the other portion was analyzed for those elements forming predominantly acidic oxides. The system provided for the detection and for the volumetric or colorimetric estimation of thirty two elements. The pedagogical advantages of the initial separation into the three major groups seemed to justify an attempt to adapt it for class use and a simplified modification of the system has been used in mimeographed form at the Institute, and with classes at the University of California at Los Angeles, for the past five years. In this system the use of the Parr bomb has been eliminated by carrying out the fusion with sodium hydroxide and nitrate in a nickel crucible. Space does not permit a more complete description of this system in this article.

As mentioned above, this system has been used with freshman classes at the Institute for several years; however, the results obtained by the class last year were far superior to those of previous classes. These students had had an opportunity during the first two quarters to acquire a background of useful techniques and an understanding of chemical equilibria which allowed them to concentrate on the descriptive chemistry of the system. The author is convinced that the potential pedagogical values of the analytical chemistry courses can be more fully exploited by beginning with simple quantitative determinations, where both techniques and principles can be developed at a reasonable pace. The qualitative work can then be done on a more rigorous and quantitative basis with respect to both theory and practice, and with more time for treatment of descriptive material.

An objective and valid appraisal of the effectiveness of this approach to the freshman laboratory work is difficult to make at present. One has to be wary of conclusions drawn from these limited experimental data, especially when psychological factors are involved. All available evidence indicated that the interest and morale of the students during the first year of this work were much better than they had been in previous years, and this improvement has been maintained during the present year. This was true in spite of the fact mentioned above, that during the first year there was a lack of correlation and synchronization between the material relating to the general chemistry text and that of the laboratory. Also, partly because of this, the amount of material presented was such as to overload seriously the average student. In spite of this, at the end of that year the number of students electing the options in chemistry and applied chemistry showed an increase of approximately 65 percent over that for any one of the previous five years. Two other factors could have been partly responsible for this effect. First, both the instructors and the students were intrigued by the participation in an experimental program. Secondly, when this work was initiated, a senior member of the staff was assigned on a voluntary basis to each of the laboratory sections. He not only exercised general supervision over the work

of the teaching assistant, but was also to spend sufficient time in the laboratory to establish a personal contact with each of the students.

The results of the first year of this work appeared to justify continuing it on an experimental basis and this is being done during the present academic year. Certain changes have been made and it is expected that this will continue to be the case as more experience is gained. At the end of the second quarter a preliminary questionnaire indicated that there will be a further gain in the number electing the chemistry options at the end of the year.

As a result of the change in the freshman course, the basic course in organic chemistry has been shifted to the sophomore year and replaces the analytical course which formerly extended through that year. This year sophomores are taking this organic course together with juniors who are under the old curriculum; there appears to be no marked difference in the performance of the two groups. The basic course in physical chemistry will be given as formerly, throughout the junior year. In the first quarter of the junior year a more advanced course in quantitative analysis will be given. This will not be an instrumentation course, but will extend the work of the freshman year to more exact measurements in the laboratory and to a more rigorous treatment of complex equilibria and of separations in the class. This course will be followed in the next two quarters by a physical chemistry laboratory course. Thus, by the end of the junior year a student will have finished his basic courses. There will be no required courses in the senior year except for those in the humanities; these compose about one quarter of the academic load of each year. The student will thus be able to take either a significant program of undergraduate research, or approved elective courses of an advanced nature in his particular field of interest. Among these approved electives are advanced courses in mathematics or in other fields of science. A significant number of students are interested in combining work in physics, biology, or geology with their chemistry option. The flexibility of this new curriculum facilitates such programs.

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