A COURSE OF INSTRUCTION

IN THE

QUALITATIVE CHEMICAL ANALYSIS

OF INORGANIC SUBSTANCES

BY

ARTHUR A. NOYES

DIRECTOR OF THE GATES CHEMICAL LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY

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QUALITATIVE CHEMICAL ANALYSIS

ARTHUR A. NOYES

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PREFACE

THIS text-book is an attempt, on the experimental side, to train the student of qualitative analysis in careful manipulation and exact methods of procedure, such as are commonly employed in quantitative analysis. It is an attempt, on the theoretical side, to make clear to the student the reason for each operation and result, and to accustom him to apply to them the laws of chemical equilibrium, and especially the principles relating to solubility and to the ionization, complex-formation, and oxidation and reduction of substances in solution. It is believed that in both these ways the educational value of the subject is greatly increased.

The book is divided into two main Parts, entitled The Course of Instruction and The System of Analysis. In presenting the System of Analysis the description of the operations is separated sharply from the discussion and explanation of them. The operations are described with as great definiteness as possible in short paragraphs entitled Procedures; and each of these is followed by Notes in which are given the reasons for the operations, the precautions necessary and difficulties encountered in special cases, the chemical behavior of the different constituents, the indications afforded of their presence, and the application of the theoretical principles to the reactions involved.

This System of Analysis is the result of many years' researches, during which the goal striven for has been gradually approached in the way illustrated by the successive editions of this book. This goal, by no means yet fully attained, has been the development of the simplest possible methods that will provide for the reliable detection of a small quantity (1 mg.) of any constituent in the presence of a large quantity (500 mg.) of any other constituent. The effort has also been made to avoid the use of tests, such as oversensitive color reactions, flame colorations, and bead tests, that do not enable the amounts of the various constituents present to be approximately estimated; for a satisfactory scheme of qualitative analysis carefully executed can be made to furnish this important information, thus often making unnecessary a more laborious quantitative analysis.

In the researches by which the System of Analysis has been brought into its present form, the author has had the able coöperation of many of his associates at the Massachusetts Institute of Technology and the California Institute of Technology. To Professors W. C. Bray and E. B. Spear belongs in largest measure the credit for the method of analysis of the aluminum and iron groups, to Professor W. C. Bray that for the alkaline-earth group, and to Professor Graham Edgar that for the detection of acidic constituents in non-igneous products as well as for improvements in many of the procedures of the copper and tin groups. The assistance and advice of Mr. Ernest H. Swift has been of great value in the final revision of the whole scheme of analysis. The author has also received many important suggestions from Professors Henry Fay, W. T. Hall, A. A. Blanchard, Edward Mueller, L. F. Hamilton, H. J. Lucas, and Mr. Roger Williams.

The Course of Instruction includes two sections — one entitled Laboratory Experiments, giving the directions for the laboratory work; and the other entitled Questions on the Experiments, consisting of a series of questions to be studied in connection with the class-room exercises.

The laboratory work described in the section on Laboratory Experiments is from beginning to end closely correlated with the systematic scheme of analysis. For experience has convinced the author that the plan followed in many text-books of requiring the student to study the separate reactions characteristic of the various elements before undertaking their systematic separation is highly unsatisfactory. However valuable the knowledge of the additional reactions might be, it is found in practice that the performance of so large a number of independent, disconnected experiments makes little impression on the student's mind and fails to awaken his interest in the subject. Qualitative analysis affords an effective means of teaching a part of inorganic chemistry chiefly because it unites into a connected whole a great variety of isolated facts, and because the student sees a practical use of the information presented to him; but these advantages evidently do not apply to facts not directly related to the process of analysis.

The Questions on the Experiments do not in general include such purely informational questions as are immediately suggested by the Notes on the Procedures. They are mainly intended to assist the instructor in training his students more fully in the general principles involved and in enabling them to derive from the subject the mental training it is capable of affording. They are in large part of such a character that, in order to answer them properly, the student must not only carefully study the Notes on the Procedures, but must also do independent thinking. It is assumed in these questions, as well as in the Notes on the Procedures, that the student has previously acquired, in his course on Inorganic Chemistry, a general knowledge of the mass-action law and of the chemical aspects of the ionic theory. To what extent the instructor will make use of the Questions will depend on the time available for the course and on the maturity of his students.

To make the course fully effective from an educational standpoint, it must be so conducted as to overcome the tendency of students to rush the laboratory experiments and to carry out the Procedures in a routine, unintelligent way. To this end the laboratory work must be supplemented by many class-room conferences with small sections of 15 to 25 students; thus there should be one such conference preceding every two laboratory exercises, or in the early stages of the course preceding each laboratory exercise, which should if possible be three hours long. The laboratory and class-room exercises should, moreover, be so correlated as to induct the student rather gradually into the detailed scheme of analysis of each group, but finally to secure by frequent repetition his full understanding of it. The best plan of doing this, in the author's opinion, involves four steps as follows: (1) Before beginning the laboratory work on any group the students are required to learn the outline of the process and the chemical reactions upon which it is mainly based, by studying the Table summarizing the analysis of that group and by reciting upon it in the class-room; but they should not be asked to learn in advance the details of the Procedures nor the contents of the Notes upon them. (2) The students then work through in the laboratory the Procedures of the group with a known solution (as described in the Laboratory Experiments), referring to the Notes, especially those with an experimental bearing. (3) They are then required to study the Notes more carefully, including those describing the principles involved, and (unless the course is a brief elementary one) to answer in writing, or prepare themselves to answer in the class-room, the corresponding Questions on the Experiments; all these matters being then taken up very fully in the class conferences, with the help of written tests, oral questioning, and explanations by the instructor. (4) After this full discussion the students review the group by analyzing in the laboratory one or more unknown solutions, as directed in the Laboratory Experiments. — In carrying out this plan it is desirable to keep the members of the class nearly together in their laboratory work, which may be accomplished by giving to the faster working students additional unknown solutions on each group, and by allowing those who are falling behind to omit some of the less important experiments, or to work overtime. In the laboratory great stress is laid on careful work, such as will enable the proportions of the various constituents present in unknown solutions to be estimated and small quantities of them to be detected. An effective means of teaching the details of manipulation, especially when the classes are large, is for the instructor to carry through in the lecture-room, after the students have had a little experience of their own in the laboratory, the complete process for the analysis of the copper-group.

Even when the time available for the subject of qualitative analysis does not permit of so complete a course as that here presented, the student gets, in the author's opinion, a better training by working through selected parts of an exact scheme of analysis carefully and thoroughly than he does by covering the whole of an elementary scheme superficially. Experiments that may be well omitted in briefer courses are indicated by asterisks prefixed to the description of them in the section entitled Laboratory Experiments.

Preface to the Ninth Edition.

This edition differs from the preceding one mainly in that it includes a comprehensive index to the whole book, in which detailed references are made to all the procedures and notes. A number of changes suggested by further experience with the book have also been made in the text; and various errors have been corrected.

Pasadena, California, January, 1922.

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TABLES OUTLINING THE SYSTEM OF ANALYSIS.

PART I

THE COURSE OF INSTRUCTION

LABORATORY EXPERIMENTS

GENERAL DIRECTIONS

Preliminary Work. — Check off on an apparatus list (corresponding to that printed in the Appendix) the apparatus found in the desk, and sign and hand in the list.

Make a 750 cc. wash-bottle, taking pains to bend the tubes and to cut them off so as to correspond closely with the model exhibited in the laboratory. Make also a 250 cc. wash-bottle (for washing with hot water and special solutions).

Make a dropper about 10 cm. (4 inches) long by drawing out one end of a glass tube to a fairly wide capillary and slightly expanding the other end with the aid of a file while it is heated in a flame. Cap the expanded end with a rubber nipple. Determine how many drops the dropper delivers to make 1 cc.; and, unless the number is within 3 or 4 of 30, widen or constrict the orifice till this is the case. Scratch on the dropper with a file a circle at the place where the volume is 1 cc.

Make 3 stirring-rods about 15 cm. long by cutting a piece of glass rod into sections and then rounding the ends in a flame.

Directions for Study. — Before carrying out each of the following experiments study the table (or other assignment) referred to at the beginning of the experiment. While making the experiment or after completing it, read the "Notes" referred to at the end of the experiment. After completing it, study the questions on it contained in the chapter entitled "Questions on the Experiments" (pages 19–38), writing out the answers to them or being prepared to recite upon them in the classroom, as the instructor may direct.

Directions as to the Note-book. — In the case of each of the experiments record in the note-book the operations very briefly; but record everything that happens fully, though concisely. Write equations expressing all the chemical changes that take place. In these equations represent solid substances by underlining their formulas, denote largely ionized dissolved substances by attaching to their formulas + and – signs in such a way as to show the ions into which they dissociate, and show slightly ionized dissolved substances by omitting these signs from their formulas. Thus the report on Expt. 1 would be made in the following form:

Expt. 1. — Added HNO_3: no change observed.
Added NH_4Cl: white curdy ppt.
$$Ag^+NO_3^- + NH_4^+Cl^- = \underline{AgCl} + NH_4^+NO_3^-.$$
Passed in H_2S: large black flocculent ppt.
$$Cu^{++}(NO_3^-)_2 + H_2S = \underline{CuS} + 2\ H^+NO_3^-.$$
. . . .

In regard to the solubility and ionization of substances, see the corresponding tables in the Appendix.

DETECTION OF THE BASIC CONSTITUENTS

Experiment 1. — *Separation of the Basic Constituents into Groups.* — Read the General Discussion on page 58, and study Table II (page 60). Measure out in a 10 cc. graduate 5 cc. portions of the test-solutions (see Note 1) of $AgNO_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, and KNO_3. Mix the portions in a conical flask, add 5 cc. of 6 n. (6 normal) HNO_3 and 4 cc. of 3 n. NH_4Cl solution, shake the mixture for a minute or two, and filter it. Dilute the filtrate with water (see Note 2) to a volume of 100 cc. Pour it into a 200 cc. conical flask; insert a two-hole rubber stopper through which passes a tube leading to the bottom of the flask; and pass in through a gas-wash-bottle a moderate current of H_2S, till, upon closing the open hole in the stopper with the finger or with a piece of glass rod, the gas no longer bubbles through the wash-bottle. Filter the mixture. To the filtrate add 10 cc. of NH_4OH and 3 cc. of 6 n. $(NH_4)_2S$ solution. Shake the mixture and filter it. Evaporate the filtrate to a volume of about 10 cc., filter, and to the cold solution add 5 cc. of $(NH_4)_2CO_3$ reagent and 5 cc. of ethyl alcohol.

Notes. — 1. The solutions of constituents to be tested for, here called the test-solutions, are all so made up as to contain 10 mg. (10 milligrams) of the constituent per cubic centimeter of solution. The mixture used in this experiment therefore contains 50 mg. of each of the basic constituents silver, copper, zinc, calcium, and potassium. The student should acquire the habit of working with definite quantities of the constituents and of noting the size of the precipitates which they yield. For a good qualitative analysis should not only show the presence or absence of the various constituents, but should also furnish an estimate of the proportions in which they are present.

Test-solutions should not be used in place of reagents, nor reagents in place of test-solutions, since the concentrations are, as a rule, quite different. Unless otherwise specified, all salt solutions used as reagents are 1 normal, and all acid or base solutions are 6 normal. The significance of the term *normal* is explained in Note 4, P. 11.

2. Distilled water should always be employed in qualitative analysis, and this is to be understood when water is mentioned.

Experiment 2. — *Precipitation of the Silver-Group. Principles relating to Equivalents, Concentration, and Solubility-Effect.* — Study P. 11 (Procedure 11 of the System of Analysis) and the Notes on it.

Prepare about 20 cc. of a 3 n. NH_4Cl solution, describing in the note-book just how it is done.

Pour into a test-tube just 10 cc. of the test-solution of $Pb(NO_3)_2$, and add from a dropper the 3 n. NH_4Cl solution, 3 drops at a time, till after shaking a precipitate remains. Calculate approximately the normal concentration of the lead and that of the chloride in the solution just before the permanent precipitate first forms, and the corresponding value of the ion-concentration product for lead chloride (assuming the salts are completely ionized). Find the ratio of this product to the saturation-value of it given in Note 6, P. 11. Let the mixture of $Pb(NO_3)_2$ and NH_4Cl stand 3 minutes; note the result, and explain it. Add to the mixture 2 cc. more of the 3 n. NH_4Cl solution, and note and explain the result.

To one drop of the test-solution of $AgNO_3$ in 12 cc. of water in a test-tube add 4 cc. of the 3 n. NH_4Cl solution. Calculate the normal concentration of silver-ion and that of chloride-ion in the solution at the moment of mixing (before the precipitate has separated), assuming that the salts are completely ionized; and find the corresponding value of the ion-concentration product for silver chloride. Calculate also the saturation-value of that product from the solubility of silver chloride given in the Table of Solubilities in the Appendix; and determine also the limit of delicacy of this test for silver by calculating the smallest number of milligrams which, if present in the solution, could have given a precipitate.

Experiment 3. — *Analysis of the Silver-Group.* — Study Table III (preceding P. 11). Mix in a conical flask 20 cc. of the test-solution of $Pb(NO_3)_2$ with 5 cc. portions of the test-solutions of $AgNO_3$ and $Hg_2(NO_3)_2$, and treat the mixture by P. 11–13. Read the Notes on P. 12–13.

* Treat the black residue left by NH_4OH by P. 14. Read the Notes on P. 14.

* *Note.* — Experiments or parts of experiments preceded by an asterisk may be omitted in brief courses on the subject when the instructor so directs.

Experiment 4. — *Precipitation by Hydrogen Sulfide.* — To 10 cc. of the test-solution of $Bi(NO_3)_3$ add 5 cc. of HNO_3, 4 cc. of 3 n. NH_4Cl solution, and 80 cc. of water; and treat the mixture as described in the second and third sentences of P. 21. Read Notes 3–5 of P. 21.

Note. — The HNO_3 and NH_4Cl are added and the mixture is diluted to 100 cc., so as to have the conditions the same as those prevailing in actual analyses.

Experiment 5. — *Effect of Acid on the Precipitation by Hydrogen Sulfide.* — Introduce into each of three test-tubes by means of a dropper 3 drops of the test-solution of $Cd(NO_3)_2$. Add to the first tube 1 cc. of HCl, to the second 3 cc. of HCl, and to the third 9 cc. of HCl. Then add to each solution enough water to make the volume about 20 cc., and pass a slow current of H_2S into it for about a minute. Repeat the last test (with 9 cc. of HCl), substituting $Cu(NO_3)_2$ for the $Cd(NO_3)_2$. Calculate the normal concentration of the HCl in each tube, and record and explain the results. Study Note 6, P. 21.

* **Experiment 6.** — *Precipitation of Arsenic by Hydrogen Sulfide.* — To 10 cc. of the test-solution of H_3AsO_4 add 5 cc. of HNO_3, 4 cc. of 3 n. NH_4Cl solution, and 80 cc. of water. Treat this mixture by the whole of P. 21, omitting the final filtration. Read Notes 7 and 8, P. 21.

Experiment 7. — *Effect of Oxidizing Substances on Hydrogen Sulfide.* — To 20 cc. of the test-solution of $Fe(NO_3)_3$ add 4 cc. of 3 n. NH_4Cl solution, 5 cc. of HNO_3, and 70 cc. of water, and pass in H_2S till the solution is saturated. Repeat this experiment, substituting 20 cc. of the test-solution of K_2CrO_4 (not the K_2CrO_4 reagent) for that of the $Fe(NO_3)_3$. Study Notes 9 and 10, P. 21.

Experiment 8. — *Analysis of the Copper-Group.* — Study Table V (preceding P. 31). Mix 10 cc. portions of the test-solutions of $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$, add 5 cc. of HNO_3, 4 cc. of 3 n. NH_4Cl solution, and 50 cc. of water, treat the mixture by the first paragraph of P. 21, and treat the precipitate so obtained by P. 31–37. Read the Notes on P. 31–37.

Experiment 9. — *Analysis of an Unknown Solution for the Copper-Group.* — Ask the instructor for an unknown solution (Unknown A) containing elements of the copper-group, and analyze 10 cc. of it for those elements. First add 5 cc. of HNO_3 and 4 cc. of 3 n. NH_4Cl solution, and treat the mixture by the first paragraph of P. 21. Treat the precipitate thus obtained by P. 31–37. Estimate the quantities present, and record and report the results, as described in the following directions.

Directions for Analyzing Unknown Solutions. — Estimate the number of milligrams of any constituent present from the size of the precipitate obtained in the Confirmatory Test or in the Procedure preceding it. In order to make this estimate more accurate, compare it, unless the precipitate is obviously very large, with that obtained by subjecting a known quantity of the test-solution directly to the same final Procedure. For this purpose use of the test-solution 0.5 cc. (measured with a dropper) in case the precipitate is small, or 5 cc. (measured in a 10 cc. graduate) in case it is fairly large, or both volumes in separate tests in case it is intermediate in size. (Note that fifteen medium-sized drops correspond to 0.5 cc., and that 0.5 cc. of the test-solution contains 5 mg. of the constituent to be tested for.) Record the analyses of unknown solutions in the note-book in three columns headed Operations, Observations, Conclusions. Enter the operations and observations in the same brief form employed in the experiments with known solutions. In the column headed Conclusions insert the conclusions that may be drawn from each observation as to the presence or absence of any of the constituents that may be present in the unknown solution; and give the estimate made of the number of milligrams present in 10 cc. of the solution. The chemical equations involved need not be written.

After the record has been written up completely in the notebook, report in duplicate the results of the analysis to the instructor in the form shown in the Note below, stating not only the nature of the constituents, but also the approximate quantities of them found present in the 10 cc. of solution. Quantities less than 5 mg. may be reported as "small" (*s*); those from 5 to 50 mg. as "medium" (*m*); and those greater than 50 mg. as "large" (*l*). (It is to be noted, since one gram of a non-metallic solid substance is ordinarily taken for analysis, that 5 mg. corresponds to the presence of 0.5% and 50 mg. to the presence of 5% of the constituent in such a substance.) The instructor will return one of the duplicate reports with an entry on it showing the quantities of the various constituents which the unknown solution actually contained.

The correctness of the results obtained in the analysis of these unknown solutions is an important factor in determining the grade of the student. As the unknowns will contain as little as 2 or 3 mg. of some constituents, satisfactory results can be secured only by careful manipulation and intelligent following of directions.

Note. — Cards with the following heading are conveniently employed for the reports of these analyses of unknown solutions, and of the later analyses of unknown solid substances; space being available below the heading for eight or ten constituents on each half of the card.

NAME. . . . . .DATE. . . . .
UNKNOWN NO. . . . . .GRADE. . . . .

CONSTITUENT	QUANT. FOUND	QUANT. PRESENT	CONSTITUENT	QUANT. FOUND	QUANT. PRESENT

Experiment 10. — *Behavior of Tin-Group Elements toward Hydrogen Sulfide and Sodium Sulfide.* — Study Table IV (preceding P. 21). To 5 cc. of water in each of four test-tubes add