

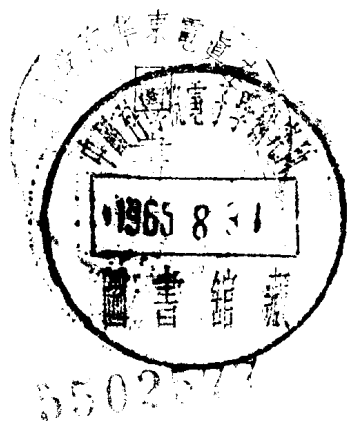
V. Alexeyev

CONTINUITY  
ANALYSIS

**V. Alexeyev**

# QUANTITATIVE ANALYSIS

**A Textbook**



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В. Н. АЛЕКСЕЕВ

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ

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## EDITORIAL NOTE

The author of this book, Vladimir Nikolayevich Alexeyev, was born in 1888 and died in 1958.

He started his practical and teaching work in the field of analytical chemistry in 1915. During the many years of his teaching activity he wrote a number of textbooks on analytical chemistry for universities and technical colleges. Besides his *Quantitative Analysis*, the books *Qualitative Analysis*, *Course of Qualitative Chemical Semimicroanalysis* and *Course of Analytical Chemistry* are well known.

In each of these books Alexeyev strove to give new facts discovered by science and to give new analytical methods, experimentally verified (in most cases by himself).

Alexeyev's books have won deserved recognition among students and teachers of Analytical Chemistry. He was always distinguished by his ability to present in simple language, logically and lucidly the fundamentals of theory and practice of analytical chemistry. Alexeyev's books have been and are being used by thousands of students, and many analytical chemists use them in their practical work.

The present book is sequel to the author's *Qualitative Analysis* and *Course of Qualitative Chemical Semimicroanalysis*. Therefore it does not deal with many theoretical questions, which are fully discussed in these books, at equal length in a course of quantitative analysis. In all such instances merely a brief mention is made of the relevant principles and results, with a reference to the appropriate sections in the textbooks of qualitative analysis.

Exceptions are made in discussion of the theoretical principles of activity, the salt effect (§ 20) and oxidation potentials (§ 78). These subjects are the most difficult for students and, moreover, they are often considered only in courses of quantitative analysis.

The author's aim was to correlate theory with the practice of analysis and, as in the textbooks of qualitative analysis, to make the theory easily understood by students.

The question of physico-chemical methods of analysis and their place in a course of quantitative analysis is a very serious problem. Only two such methods are considered in detail in the book: colorimetry (visual) and electrogravimetric analysis. Conductometry, potentiometry, polarography, and photolorimetry are considered only in outline, without descriptions of the methods or examples of determinations.



CHAPTER I  
INTRODUCTION

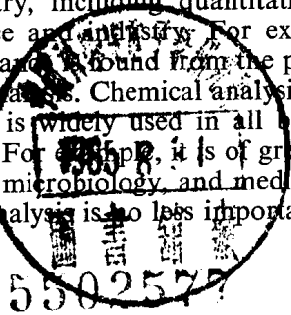
§ 1. The Subject of Quantitative Analysis .

Analytical chemistry is divided into two parts, qualitative analysis and quantitative analysis. Qualitative analysis shows what elements (or ions) a given substance contains. The aim of quantitative analysis is determination of the quantitative contents of individual elements or compounds present in a substance.

Analytical results are usually expressed in percentages. For example, in analysis of calcium carbonate it is found what percentages of calcium, carbon and oxygen it contains. In view of the fact that  $\text{CaCO}_3$  may be regarded as a compound of calcium oxide  $\text{CaO}$  with carbonic anhydride  $\text{CO}_2$ , the composition of this salt is also often expressed in percentages of the oxides  $\text{CaO}$  and  $\text{CO}_2$ .

Sometimes the determination of the total contents of individual elements (or their oxides) in a sample is insufficient and it is also necessary to know in the form of what compounds these elements are present and what the relative proportions of these compounds are. For example, carbon may be present in ferrous alloys both in the free state, as graphite, and in the combined state, in the form of carbides. The properties of an alloy greatly depend on the form in which carbon is present. Therefore, in addition to the total carbon content the amounts of free and bound carbon in an alloy are also sometimes determined. In the same way, in analysis of clays or bauxites in addition to the total contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , chemically bound water, etc., it is also necessary to find how much  $\text{SiO}_2$  is present as quartz and how much in the form of various silicates. Determination of individual compounds present in a given substance is known as *phase analysis*. In phase analysis the compound to be determined is first separated (for example, by making use of different behaviour towards solvents or differences of various physical properties) from other compounds of the same element present in the substance, and the compound is then analysed.

Analytical chemistry, including quantitative analysis, is of enormous importance in science and industry. For example, the chemical formula of an unknown substance is found from the percentage contents of its constituents, found by analysis. Chemical analysis is a most important method of investigation and is widely used in all branches of science which are related to chemistry. For example, it is of great importance in mineralogy, geology, physiology, microbiology and medical, agricultural and technical sciences. Chemical analysis is no less important in industry. The technolo-



gist must know at every stage of the production process both the qualitative and the quantitative composition of the materials undergoing conversion. For example, a furnace charge in the production of cast iron or glass can be made correctly only if the composition of the charge materials is known; for most efficient leather tanning the contents of tanning materials in the extracts must be known, etc.

At the present time no material is taken into production or released without analytical data which characterise its quality and suitability for various purposes. These results not only form the basis of all the processing calculations but they also determine the costs of the materials, which form the basis of financial estimates.

Analysis of intermediate products (for example, smelting control in metallurgy, etc.) is of enormous importance. The technologist uses the results of such analysis for the most efficient utilisation of the raw material, for prevention of troubles in the course of the process and therefore for prevention of spoilage.

The great importance of proper chemical control of production is obvious. Therefore, in nearly every factory one of the most important sections is the analytical laboratory for chemical control of production.

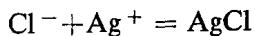
When quantitative analysis is undertaken, the qualitative composition of the given substance must be accurately known; qualitative analysis must be used even if the presence of a particular element in the substance is definitely known, because the correct method for quantitative determination of the element in question can be chosen only if the qualitative composition of the substance is known.

In practice, however, the analyst's problem is usually simplified considerably, because the qualitative composition of most of the investigated substances (ores, alloys, fertilisers, etc.) is well known. Approximate contents of individual elements are also quite often known.

Obviously, in such cases not only is preliminary qualitative analysis unnecessary, but the choice of the most suitable method of quantitative analysis becomes very much easier.

## § 2. Methods of Quantitative Analysis

The same ionic reactions as are used in qualitative analysis are generally utilised in quantitative analysis. For example, chlorine (or, more correctly, chloride ion) is determined quantitatively by precipitation by silver ions:



Chlorine content may be determined by various methods on the basis of this reaction. For example, the precipitated AgCl can be filtered off, washed thoroughly, carefully heated (or dried) and accurately weighed. From the weight of the AgCl precipitate and its formula it is easy to calculate its chlorine content.

Thus, in the analysis of 0.0536 g NaCl the precipitate weighed 0.1290 g; since one gram-molecule (i.e., 143.3 g) AgCl contains one gram-atom (i.e., 35.46 g) Cl, we can write:

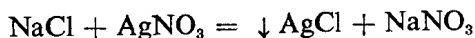
$$\begin{aligned} 143.3 \text{ g AgCl} &\text{ contains } 35.46 \text{ g Cl} \\ 0.1290 \text{ g AgCl} &\text{ contains } x \text{ g Cl} \\ x &= \frac{0.1290 \times 35.46}{143.3} = 0.03193 \text{ g Cl} \end{aligned}$$

Since all the chlorine was originally present in the weighed samples of common salt (NaCl) the percentage chlorine content of the latter is easily found:

$$\begin{aligned} 0.0536 \text{ g NaCl} &\text{ contains } 0.03193 \text{ g Cl} \\ 100 \text{ g NaCl} &\text{ contains } y \text{ g Cl} \\ y &= \frac{0.03193 \times 100}{0.0536} = 59.6\% \end{aligned}$$

This method is known as *gravimetric analysis*, because the weight of the reaction product is used for finding the amount of an element present.

The amount of chlorine in common salt can also be found in another way, by means of *titration*, i.e., measurement of the volume of a reagent solution (AgNO<sub>3</sub>) of accurately known concentration, required to precipitate the Cl<sup>-</sup> ions. These two quantities—the volume and the concentration of the reagent solution—are quite sufficient to calculate the chlorine content of the substance. For example, if 18.00 ml of AgNO<sub>3</sub> solution 1 ml of which contains 0.0085 g of this salt was required to precipitate all the chlorine in a solution of a weighed sample in water, then obviously the amount of AgNO<sub>3</sub> taken for the whole reaction is 18.00 × 0.0085, i.e., 0.1530 g. The equation for the reaction



shows that to precipitate one gram-ion (i.e., 35.46 g) of Cl one gram-molecule (i.e., 169.9 g) of AgNO<sub>3</sub> is required. Therefore we can write:

$$\begin{aligned} \text{precipitation of } 35.46 \text{ g Cl} &\text{ takes } 169.9 \text{ g AgNO}_3 \\ \text{precipitation of } x \text{ g Cl} &\text{ takes } 0.1530 \text{ g AgNO}_3 \\ x &= \frac{0.1530 \times 35.46}{169.9} = 0.03193 \text{ g Cl}^* \end{aligned}$$

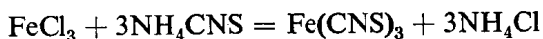
Then, as before, it only remains to calculate the percentage of chlorine in the samples.

The method based on accurate measurement of the volume of a reagent solution of accurately known concentration, taken for a reaction, is known as *volumetric analysis*.

\* Other and more convenient calculation methods will be considered later. They are discussed in § 56.

In volumetric determinations it is evidently necessary to establish exactly the end point of the reaction; this is not always possible. Moreover, the reaction itself must satisfy a number of conditions, and therefore the applicability of volumetric analysis is more restricted than that of the gravimetric method. An important advantage of the volumetric method is its greater speed, which is very important in practice, as for example in chemical control of production.

Reactions accompanied by colour changes are often used in qualitative analysis. For example, when the  $\text{Fe}^{+++}$  ions are detected by means of  $\text{NH}_4\text{CNS}$  or  $\text{KCNS}$ , soluble iron thiocyanate  $\text{Fe}(\text{CNS})_3$  of a deep red colour is formed:



This reaction can also be used in quantitative analysis. By this method the unknown solution and a "standard solution", i.e., a solution of a ferric salt of accurately known concentration, are treated with  $\text{NH}_4\text{CNS}$  or  $\text{KCNS}$  under the same conditions. If both solutions give the same colour, then the content of  $\text{Fe}^{+++}$  must also be the same. If the colour of the unknown solution is deeper (or less deep) than that of the standard, then the concentration of  $\text{Fe}^{+++}$  ions in it must be higher (or lower) than that of the standard.\* The analytical method based on comparison of colour intensities is known as *colorimetric analysis*.

Instead of reactions involving colour changes, reactions accompanied by formation of sparingly soluble substances are sometimes used. The amount of a given element in solution is estimated from the degree of turbidity of the solution produced by some reagent or other, compared with the turbidity of a corresponding standard solution. Methods based on this principle are known as *nephelometric*.

Colorimetric (and nephelometric) determinations are possible only if the colours (or turbidities) of the solutions are not too intense. Extremely dilute solutions are used for such determinations. In practice the colorimetric and nephelometric methods are most commonly used when the content of the unknown element in the material is very low and therefore the gravimetric and volumetric methods are unsuitable. Colorimetric methods are also used widely because of their high speed.

Several other methods are used in quantitative analysis. For example, we must mention *gas analysis*, which generally consists in determining the volumes of individual components in a gas mixture, for example, by absorption in various reagents. The decrease of the gas volume is a measure of the absorbed component. There are also volumetric methods of gas analysis, in which the amount of an element is found by measurement of the volume

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\* This is only true for fairly dilute solutions. The eye cannot distinguish differences between intensely coloured concentrated solutions.

of gas formed in a reaction. For example, carbon in iron or steel is usually determined from the value of  $\text{CO}_2$  formed in combustion of a weighed sample in a current of oxygen at 1,000-1,250°C in a special electric furnace.\*

*Electrogravimetric analysis* is widely used (especially for analysis of non-ferrous metals and alloys). In this method the element (in the free state) is isolated by electrolysis on a previously weighed electrode (certain elements are liberated in electrolysis in the form of oxides, such as  $\text{MnO}_2$  or  $\text{PbO}_2$ ). The increase in the weight of the electrode shows the amount of the element liberated.

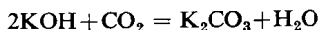
There are also methods of *electrovolumetric analysis*, which are based on the usual principle of volumetric determinations (see above) but the end point of the reaction is established either by measuring the electrical conductivity of the solution (*conductometric method*), or by measuring the potential of an electrode immersed in the solution (*potentiometric method*). The electrochemical methods also include the so-called *polarographic method*. In this method the amount of an element (or ion) in a solution is estimated from the character of the volt-ampere curve (or "polarogram"), obtained in electrolysis of the solution carried out in a special apparatus known as a polarograph.

Mention must also be made of analytical methods based on the use of *labelled atoms*, i.e., radioactive isotopes of the elements to be determined. The fact that these isotopes are radioactive, while their properties are identical with the properties of the corresponding stable isotopes, makes it possible to use counters which measure various radiation intensities. It is then very easy to solve problems which are very difficult and sometimes impossible to solve by the usual analytical methods. The following example illustrates this. In order to find how phosphorus is distributed between metal and slag in the smelting of steel, calcium phosphate containing the radioactive phosphorus isotope with a half-life of 14.3 days is introduced into the smelting furnace. Samples of metal and slag are taken during the smelting and their radioactivity is determined by means of a counter. This gives a rapid and easy answer to the problem of the distribution of phosphorus between steel and slag, and the factors on which this distribution depends. The labelled atom method is extremely sensitive which is another of its valuable characteristics.

Another method used in analytical practice is the *chromatographic method*. This is based on selective adsorption of dissolved substances or ions by various solids (adsorbents), such as aluminium oxide, permutite, various syn-

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\*To measure the volume of  $\text{CO}_2$  formed, the gas mixture  $\text{CO}_2 + \text{O}_2$  leaving the furnace is passed through a concentrated  $\text{KOH}$  solution which absorbs  $\text{CO}_2$ ; the reaction proceeds according to the equation:



The decrease in the volume of the gas mixture shows the amount of  $\text{CO}_2$ .



thetic resins, etc. Chromatography is particularly valuable for separation of various substances or ions. Experience shows that even slight differences in the composition or structure of substances are usually enough to cause considerable differences in their adsorption. Because of this the chromatographic method can be used for separating substances which are so similar in properties that they cannot be separated by other methods or are only separated with great difficulty.

All the above methods of quantitative analysis can be divided into *chemical* and *physico-chemical methods*. The former group includes gravimetric, volumetric and gas analyses and the second group includes colorimetric, nephelometric, electrochemical and chromatographic analysis.

In addition there are *physical methods* of quantitative determination, such as quantitative spectroscopic analysis, luminescence analysis, etc.

Both in quantitative and in qualitative analysis a distinction is made between macro-, micro-, and semimicromethods.

In *macroanalysis* relatively large samples (about 0.1 g or more) of solids or large volumes (tens of millilitres or more) of solutions are taken.

The essential instrument for this method is the analytical balance, which can be used for weighing to an accuracy of 0.0002 g (or 0.2 mg).

In addition to the macromethod, micro- and semimicromethods of quantitative analysis are coming into increased use. In these methods samples weighing between 1 mg and 50 mg and solution volumes between tenths of a millilitre and several millilitres are used.

In such cases, to obtain the necessary accuracy it is necessary to use a more sensitive balance, such as a microbalance (accurate to 0.001 mg) and more accurate apparatus for measurement of solution or gas volumes. The main advantages of the micro- and semimicromethods are their high speed and the need for only very small amounts of material. Despite these advantages the classical macromethod, which is the oldest and the most convenient method of quantitative analysis is the one most widely used at the present time.

Only the methods of quantitative macroanalysis are considered in this book.

### § 3. The Analytical Balance

The balance is the principal instrument used in quantitative analysis. The analytical results obtained by any method must be referred to a definite quantity of the given substance; for example, as a percentage of its weight. Therefore, the first stage in analysis is usually to weigh out a definite portion (sample) of the substance for investigation.

Weighing is also used in other operations of quantitative analysis; for example, to find the weight of a precipitate, to prepare solutions of accurately known concentration, etc.