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Introduction

The Task of Qualitative Analysis

The purpose of qualitative analysis is the discovery of the essential nature of the object under investigation. A procedure of qualitative analysis, which shall be useful in actual analytical practice, must be generally applicable. It must give information without regard whether the object is a mixture or a pure substance; rare or common; simple or complex; organized, organic or inorganic; and whether it is known and described or as yet "unknown" and not yet mentioned in the literature. In addition to this, the procedure must be applicable to very small amounts of sample since qualitative analysis is frequently needed to determine the nature of minute objects.

It is impossible to ever present a complete practical scheme of qualitative analysis between the covers of a book since the practicing analyst may have to draw on any and every part of our knowledge of material things. A sensible approach, however, will give some useful information under all conditions and at the same time provide a high probability that simple problems will be solved satisfactorily and efficiently. The amount of information that can be gained with a suitable scheme will depend on the nature of the object. Obviously, qualitative identification must fail whenever distinguishing features are missing, and it may be impossible to indicate more than the general class of matter (lanthanides, mixture of fatty acids, proteid substance).

It is also plain that lack of material may seriously limit the scope of investigation and the amount of information that can be gained. Assuming, however, the existence of suitable apparatus and technique (145), one may say that the amount of material available for testing is only a minor factor in estimating the difficulty of the task. The time and labor needed depend in the first place upon the amount of information available concerning the sample and upon the amount of knowledge to be gained by the analysis. Under otherwise equal conditions, it will depend mainly upon the complexity of the object of investigation and upon the number and kind of separations required, whereby the emphasis should be on the latter since the number of constituents in the sample is by far not as important as their nature and their mass ratios.

If the object is a substance which is not yet described in the literature (146), qualitative analysis may or may not reveal this fact. It may furnish

descriptive material, possibly some data concerning physical and chemical properties, the elemental composition as to kind, and perhaps evidence concerning functional groups and the general class of substances to which it belongs. As a rule, however, precise determination of percentage composition, number of functional groups, molecular weight, etc., are required to give a new substance its proper name, i. e., to assign it the correct niche in our classification of matter. If some unique behavior, physical or chemical, is discovered in the course of the investigation, this will facilitate the recognition of the substance when it occurs again.

This book outlines a plan of investigation for the use of the practicing chemist. Emphasis is placed upon a proper start which assures accumulation of useful information with small expenditure of sample material and the quick identification of common simple materials. References to the literature serve to widen the field of investigation in all directions toward the limits of our knowledge. Descriptions of technique are included to permit the investigation not only of small samples but of truly minute objects.

Principles and Definitions

In the strict sense, analysis (ἀνάλυσις = resolution) should apply only to the method of taking apart or breaking down things for the purpose of investigation. Destruction of the sample, however, is not necessarily a part of qualitative analysis.

The modifier *qualitative*, too, should be accepted with a rather loose meaning. It indicates that no effort will be made toward a precise determination of the mass ratios if it should turn out that the sample is a mixture of several chemical specimens. On the one hand, the purely "qualitative" finding that the sample consists of sodium chloride implies the quantitative facts that it is composed of 60.67 per cent chlorine and 39.33 per cent sodium and represents practically 100 per cent of the combination of the two. On the other hand, a statement that the sample consists of sodium, calcium, sulfate, chloride, and water would not permit identifying the object of analysis. It could be gypsum contaminated by some rock salt, or table salt contaminated with gypsum, or some hydrate of calcium chloride mixed with some sodium sulfate, or a concentrated or dilute solution of some combination of the four possible salts, etc. Obviously, an approximate statement of the ratio of the ingredients is required before the object of investigation can be given a name; a merely qualitative statement does not suffice in such instances where several chemical specimens are found in the sample.

The primary task of qualitative analysis, the disclosure of the general nature of the sample, is usually accomplished by a rather crude classification according to mass ratio. Customarily one distinguishes *majors* (more than

5 per cent of the whole), *minors* (between 0.1 to 5 per cent), and *traces* (less than 0.1 per cent of the whole).

Whereas observations of mass ratios are frequently required, the performance of laborious quantitative determinations is avoided since the *general nature* of the object, as a rule, may be recognized without precise knowledge of ratios. In most instances it will suffice to know the major and minor constituents. A more exacting qualitative task, the *identification* of a special steel, of a special batch of copper, or of a reagent taken from a certain bottle, etc., may be solved by a study of the trace constituents or may require precise quantitative determinations.

There is no sharp dividing line between analysis and micro analysis. One speaks of **micromethods** whenever the experimentation proceeds with significantly less material than is customarily used for the purpose. If "significantly" is translated to mean ten times, there still remains the interpretation of "customarily", which will change with time and circumstance. In addition, there is the fact of the continuously varying amount of matter (sample) taken for testing. Schemes of separation for inorganic qualitative analysis usually start with one decigram to one gram of sample, but only milligrams and fractions of milligrams are used for the final confirmatory tests; the quantities decrease even to micrograms when flame tests, spot tests, fluorescence phenomena, etc., are included among the final tests.

By **sample** is always meant that part of the object of investigation, which is being treated or observed at the particular stage of experimentation. It is always assumed that it is truly representative of the whole object.

Because of the impossibility of giving a precise meaning to the term micro and derived terms, EMICH suggested to indicate the **scale of work** by stating the approximate mass of the sample used at the time. The magnitude of mass is indicated with the use of the prefixes of the metric system. Accordingly one may state that schemes of separation in inorganic analysis are customarily started on a decigram or gram scale, whereas preliminary tests and confirmatory tests are carried out on either the centigram, milligram, or submilligram scales. If the total amount of sample required or the amount of sample required for the separation of cations (these two quantities are in the approximate ratio of two to one) is taken for criterion, the terms semimicro, micro, and ultramicro may be interpreted as refering to inorganic qualitative analysis with decigram, milligram, and microgram samples, respectively.

The subdivision into inorganic and organic analysis complies with the fact that the limitations of human capability call for specialization. Since the objects of analysis are not necessarily labelled organic or inorganic, a procedure must be followed that leads to the recognition of organic substances in time so that the task may be turned over to a specialist if

the already established facts and some additional simple tests, which are recommended, do not suffice for a solution of the problem. The practical analyst cannot adopt the rules of game of the typical school texts on qualitative analysis, which restrict the search to a small selection of inorganic cations and anions and may even require that the sample for analysis is an aqueous solution of a certain concentration range.

Specificity and Sensitivity

So far, chemical reactions cannot be observed as such. The objects of observation are the physical properties of the reacting system before, during, and after the reaction. The reactions used for recognizing substances produce either one or both of the two following effects:

a) Changes affecting the transmission of light by the appearance or disappearance of phases (boundary lines): changes from homogeneity to heterogeneity and vice versa. Into this category belong precipitation, evolution of gas, dissolution, condensation, evaporation, transition to a different state of aggregation, etc.

b) Distinct changes affecting the absorption or emission of light, i. e., changes of color, fluorescence, phosphorescence.

The practical value of an analytical test or procedure depends mainly upon the nicety of discrimination, its selectivity, and upon the limiting proportions. Tests (procedures, reagents) to which only one substance responds are called **specific**. Tests which are given only by a small number of substances are classified as **selective** (1241).

Sensitivity of a test (procedure, reagent) is to be described by listing the limiting concentration, the limit of identification, and the limiting proportions (850). The first two usually apply only in the absence of interfering substances and become less favorable in the presence of such.

The **limiting concentration** (L. C.) is defined as the lowest concentration of substance which always produces a positive test. Its dimension is mass per volume (856, 859).

The **limit of identification** (L. I.) is the smallest absolute quantity (mass or volume) which always gives a positive test (850).

The **limiting proportions** (L. P.) are the smallest mass ratios (substance sought/substance interfering) which still always permit to get a positive test (1137).

If perceptibility, the limitation imposed by our senses, is not considered, one may assume that limiting concentrations and limiting proportions are determined by essentially chemical phenomena: rate of reaction, shift of equilibrium, side reactions, establishment of metastable equilibria, complex formation, catalysis, solubility, coprecipitation, etc. Thus it is reasonable to expect that limiting concentrations and the important limiting proportions will not depend upon the size of the reacting system.

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This assumption is supported by the available evidence, and it may be expected that the limiting proportions (and limiting concentrations) determined for gram samples will also hold on the microgram or nanogram scales and *vice versa*. The limits of identification, of course, depend upon the absolute size of the sample or the volume of solution taken for the test and may be improved by reducing the scale of work. The relation L. I. = = L. C. × volume should hold within a considerable range.

As a rule, the limiting proportions are less favorable than the limits of identification or limiting concentrations which apply only after the substance has been isolated in a more or less pure state. It is important to realize that negative confirmatory tests must be interpreted with reference to the sensitivity criteria. A negative test does not prove more than that the amount of substance, if it should be present, is less than indicated by the limit of identification or limiting proportions. If separations have preceded the test, the criterion is provided by the operation with the least favorable limiting proportion. Absence in an absolute sense cannot be proven by an analytical test; at times, it may be concluded from the history of the object under investigation.

Limiting concentrations, limits of identification, and limiting proportions cannot be determined with high accuracy since the conditions which always give a positive test and those which always lead to a negative result have no sharp borderline. They are separated by a range of conditions, which produces uncertainty as to the outcome: some trials give positive and some negative results (22, 150, 1580). This implies that the limiting conditions "always" leading to a positive result must be established by a sufficient number of experiments.

Suggestions for the brief notation of sensitivity criteria originated with GILLIS (899), FLASCHKA (341), and MALISSA (895, 898). For this book, the simple notation according to HAHN (962) has been adopted:

a) If a solid sample is being tested, the exponent (negative logarithm) of the limit of identification given in gram, pL. I., is listed in parenthesis: (6.0).

b) If a solution is being tested, the parenthetical notation indicates the subtraction pL. C. — pL. I.: (4.0 — 7.0), whereby the L. C. is given in gram per milliliter and the L. I. in gram. Performance of the subtraction leads to the logarithm of the volume of test solution given in milliliter: 0.001 ml = 1 μl. The notation consequently reveals also the scale of performance.

c) To indicate the limiting proportions, the interfering substances are listed with the logarithm of their limiting mass per unit mass of substance tested for:

(6.0; Fe, Co, Ni: 2; U: 1) means that 1 μg of X may still be detected in presence of 100 μg of Fe, Co, or Ni and in presence of 10 μg of U.

(4.2 — 7.5; Ca: 2.5) indicates that 0.03 μg X, L. C. = 60 μg X/ml, may be detected in a drop of 0.5 μl in presence of 9 μg Ca.

HAHN suggests to give the figures with one decimal.

The Method of Qualitative Analysis

Two *principal steps* may be recognized when considering the performance of a qualitative analysis (463): the *preliminary treatment* of the sample material and the *performance of the tests* that identify the substances which are present. This classification applies whether all tests are performed on one portion of the sample, or various tests require separate portions of the sample; in either instance, the material taken for analysis usually must undergo some treatment before the decisive tests may be applied.

The final tests, which are known as *confirmatory tests*, obviously must be based upon the observation of some phenomenon that, under the prevailing conditions, is produced only by the substance under consideration. The observed phenomenon may originate with a chemical, physical, or biological property that is characteristic of the substance (145); the intensity of the phenomenon is usually directly related to the mass of substance so that a crude estimation of quantity becomes possible. As a rule, confirmatory tests as well as estimations of quantity may be performed quite rapidly and without difficulty, once substances have been obtained in a reasonably pure state.

The *treatment* of the sample material *preliminary to* the *confirmatory tests* may involve transfers, disintegration, mixing, aliquot partitions, preparation of solution(s), and involved procedures for the separation of constituents. It may require nothing beyond transfer of the sample or part of it to some apparatus for treatment or observation if either the sample has a simple composition, or very specific and sensitive tests are available for obtaining the desired knowledge. It should be considered in this connection that the task may require merely a decision on absence or presence of a certain substance.

Whenever little or nothing is known concerning the nature of the sample, its composition is more or less complex, and sensitive as well as specific tests are missing, then it becomes necessary that isolation precede the identification of the various constituents. Isolation implies separation and transfer in space, i. e., mechanical operations which require that the substances to be separated have been collected in different phases.

Separable phases may exist to begin with. As a rule, however, they must be established for the purpose of separation. Only three ways are available for the creation of a phase: (1) the phase may be added mechanically; (2) it may be caused to appear as a consequence of a change in temperature or (and) pressure; and (3) it may be made to separate as the product of a chemical reaction proceeding in the system. Obviously, one will try

to obtain a new phase of such a kind that some of the substances to be separated collect in it in their entirety, whereas the others remain altogether outside of it. Noticeable deviations from this ideal are quite common as a consequence of finite distribution ratios as well as adsorption phenomena and are responsible for the difficulty of getting perfect separations.

Apparatus and manipulative technique for the purely mechanical part of the separations must depend upon the nature of the phases to be separated. The three states of matter give five combinations which represent the natural divisions for a discussion of mechanical separations: solid-solid, solid-liquid, solid-gas, liquid-liquid, and liquid-gas. When suitable apparatus and proper techniques are applied, the purely mechanical part of the separations should not introduce errors or cause losses of a magnitude that would render them significant in qualitative analysis.

The Minimum Size of the Sample for Chemical Analysis

The various species of matter are identified by their properties. Obviously, the microchemist must be concerned about the effects of diminishing size upon the properties of matter and the means for their observation.

It follows from the atomistic concept of matter that its properties should remain unchanged down to the size of the fundamental units. These already contain the correct kind, ratio, and arrangement in space of the building stones, that determine the particular behavior. Therefore, the fundamental unit should represent the size of the smallest sample suitable for the study of physical properties since the particular material and the properties belonging to it cannot exist in a still smaller quantity of matter. Masses larger than the fundamental unit are simply accumulations of the latter and should not present any novel features excepting incidental phenomena such as size and shape, that can be assumed by any material.

The size of the fundamental unit that still permits qualitative identification on the basis of the typical properties depends greatly upon the type of material. In the instance of a coarse conglomerate, it may take a piece of several kilograms to reveal the essential characteristics; with crystalline rocks, a fraction of a gram may be required. The fundamental unit of mixtures must represent a reasonably close approximation of the composition of the whole (13, 14). Of suspensions, emulsions, colloidal sols, and molecular dispersions, a volume will be required which includes a fairly characteristic percentage of the dispersed matter. In the instance of chemical specimens (substances) the fundamental unit may be identified with the molecule or the unit cube of a crystal lattice.

When dealing with chemical specimens (solids and liquids), the fundamental unit representing the critical limit to identity and identification

can hardly be imagined to exceed 1000 atoms corresponding to a mass of $1000 \times 1.7 \times 10^{-24} W$ gram or 3.4×10^{-19} gram if an average molecular weight is assumed such as $W = 200$.

After remembering that the energy content of one molecule or one fundamental unit need not represent the temperature of the bulk and that the collision of light with just one fundamental unit may not lead to the commonly accepted value for the refraction, one may be inclined to take into account the essentially statistical nature of the phenomena exhibited by matter. Accordingly one may adopt a safety factor of 1000 and expect that this number of fundamental units would give a satisfactorily close approach to the average effects observed with large quantities of matter and thus permit identification by observation of the characteristic behavior with about 10^{-15} to 10^{-16} g (0.003 pg) of substance (145).

There is no doubt that such and smaller quantities will suffice for identification if the phenomena are striking and originate in the atom or in the molecule. Thus it has been assumed long ago (1149) that quantitative determinations via the radiation count are possible with 10^{-15} g of highly radioactive elements, which implies that one hundredth of this amount or less (10^{-17} to 10^{-18} g) should suffice for qualitative identification. EMICH (150) demonstrated that 10^{-15} g hydrogen are sufficient to produce the line H_α, and PANETH and PETERS (652, 1201) devised gasvolumetric apparatus that permitted to identify 2×10^{-14} g helium by means of the glow discharge. With the use of the microscope, fluorescence may be studied on tiny objects; thus taking hemispherical drops of 1-μm (μ) diameter, one should be able to recognize 2.5×10^{-16} g fluorescein in 0.1 per cent solution.

It appears safe to assume that general theoretical reasoning permits reducing the scale of chemical experimentation to 0.001 pg $= 10^{-15}$ g of mass and possibly less. One may expect with quantities down to this limit that matter still has the customarily accepted values for density and specific volume, refraction, optical rotation, absorption of radiation, magnetic susceptibility, conductivity, electrode potential, etc. One may also expect that the customarily known equilibria will establish themselves in reaction mixtures down to this size. This has important practical consequences.

In most microchemical work, one is very far from approaching the *critical size limit*. Therefore one may feel certain that there will be no fundamental change in physical properties and in chemical equilibria when the available quantity shrinks to milligrams, micrograms, nanograms, or picograms. Since equilibria are determined, aside from temperature and pressure, solely by the concentration of the reactants, working *directions* may be simply *transposed* from anyone scale to any other by multiplying all weights and volumes with the same factor and retaining concentrations,

temperatures, and pressures without change. Any test or scheme of separation may be carried out with micrograms exactly as described for the gram scale by just reducing all weights and volumes to one millionth, by taking micrograms instead of grams, nanograms instead of milligrams, and nanoliters in place of milliliters. Experiences gained on any scale hold for every other scale of work; the utilization depends merely upon application of proper techniques in observation and experimentation. The "chemistry" and the theory of qualitative analysis may be applied as found in the general literature (13—82).

It has been demonstrated by RACHELE (424) that the critical size limit may be closely approached by the suitable performance of common test tube tests. Droplets of test solution and reagent solution were deposited by means of a micromanipulator in a film of paraffin oil that had been deposited upon the underside of the top plate (cover slip) of a moist chamber. The operation was performed in the field of a high-power microscope so that it was possible to measure the diameter of the spherical drop of test solution and to ascertain that both drops were clear. Drops of different size merged spontaneously if deposited close to each other, whereupon the separation of a precipitate or the development of a coloration was observed. Thus the limit of identification was reached with 10^{-14} g of barium ion supplied in a drop of 1 pl (12 μm diameter) of 0.001 per cent solution. With magnifications of about 400 diameters, a fine crystalline precipitate could be observed with transmitted light as well as with dark-field illumination. The Prussian blue test was reliably obtained with 0.4 pg of ferric ion supplied by drops of 4-μm diameter (0.04 pl volume) of 1 per cent solution. In a like manner, ANNA G. LOSCALZO (1261) could identify 0.02 pg silver as silver chloride, 0.2 pg cobalt as cobalt-mercuric thiocyanate, and 0.5 pg iron as ferric thiocyanate.

In all instances it was felt that the phenomena were probably obtained with still smaller quantities, but that it became impossible to observe them with the means employed.

Properties Affected by the Size of the System

It is to be expected that all properties that do not reside in the fundamental unit may vary with the amount of matter. Thus all statistically established equilibria must be affected even though our insufficiently precise methods of observation fail to reveal the differences.

Most of all one may expect to find deviations from the customary experience with properties or equilibria acting on or across phase boundaries. This is to be expected because the relative amount of surface must increase when mass and volume diminish.

It may be readily demonstrated that the **specific surface area,** defined as surface area per unit volume, A/v, must be inversely proportional to

the cube root of the volume (or mass) provided that the shape and its proportions are retained. In the instances of the tetrahedron, the cube, and the sphere, the equations are $A/v = 7.2/v^{1/3}$ (tetrahedron), $A/v = 6/v^{1/3}$ (cube), and $A/v = 4.8/v^{1/3}$ (sphere).

The decrease of mass and volume and the corresponding increase of specific surface area affect the surface tension and as a consequence the vapor tension, solubility, melting point, and boiling point. The changes are insignificant until the particle diameters drop below 1 μm, i. e., the volume below 10^{-12} ml and the mass below 10^{-11} to 10^{-12} g. Noticeable increases of vapor tension and solubility are expected with decidedly smaller amounts of matter.

In the instance of barium sulfate, DUNDON (22) estimates a nearly hundredfold increase of the solubility when the diameter of the particles dropped to 0.4 μm corresponding to a mass of a cube-shaped particle of 3×10^{-13} g. The solubility should have been still higher in the experiments of RACHELE (424) where only about 2×10^{-14} g of barium sulfate were available at the limit of identification. The published photomicrograph indicates at least four large particles, and if five of them were present, their diameter could not have exceeded 0.1 μm. RACHELE, however, assumes that these particles were aggregates and that a large number of still finer particles collected at the interface with the paraffin oil. The findings are not necessarily in contradiction. Aside from the fact that there is no definite assurance concerning the absence of finer particles in the experiments of DUNDON, excess of sulfate ion in RACHELE's tests may have more than compensated for increased solubility. Finally, somewhere near the critical size limit, there must be some reversal in the solubility-particle diameter relation to permit the formation and growth of nuclei.

In addition to these effects, a large specific surface area may have a noticeable *influence* upon *the composition* of matter. In the instance of a palpable collection of matter (crystalline or liquid), the mass of the substances adsorbed on the surface may be alltogether negligible when compared with the bulk. The ratio of adsorbed foreign matter to the mass of the bulk must increase, however, when the latter diminishes. If the mass decreases to include just a small number of unit cubes or molecules, one may very well imagine that the amount of adsorbed matter could assume such a proportion as to change the identity of the accumulation. If no precautions are taken, adsorption might materially affect the performance of chemical separations on a very small scale. Fortunately, however, adsorbed matter is, as a rule, readily removed by washing or displacement.

So far, microchemical experimentation has produced no evidence of a change of chemical or physical behavior as compared with that customarily

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