QUANTITATIVE AGRICULTURAL ANALYSIS

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INTERNATIONAL ATOMIC WEIGHTS

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminum	Al	26.97	Mercury	Hg	200.61
Antimony	Sb	121.77	Molybdenum	Mo	96.0
Argon	A	39.91	Neodymium	Nd	144.27
Arsenic	As	74.96	Neon	Ne	20.2
Barium	Ba	137.37	Nickel	Ni	58.69
Beryllium	Be	9.02	Nitrogen	N	14.008
Bismuth	Bi	209.0	Osmium	Os	190.8
Boron	B	10.82	Oxygen	O	16.00
Bromine	Br	79.916	Palladium	Pd	106.7
Cadmium	Cd	112.41	Phosphorus	P	31.027
Calcium	Ca	40.07	Platinum	Pt	195.23
Carbon	C	12.00	Potassium	K	39.096
Cerium	Ce	140.25	Praseodymium	Pr	140.92
Cesium	Cs	132.81	Radon	Rn	222.0
Chlorine	Cl	35.457	Radium	Ra	225.95
Chromium	Cr	52.01	Rhodium	Rh	102.91
Cobalt	Co	58.94	Rubidium	Rb	85.44
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.43
Dysprosium	Dy	162.52	Scandium	Sc	45.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.06
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	22.997
Gallium	Ga	69.72	Strontium	Sr	87.63
Germanium	Ge	72.6	Sulfur	S	32.065
Glucinum	Gl	9.02	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.4	Thallium	Tl	204.39
Hydrogen	H	1.008	Thorium	Th	232.15
Hafnium	Hf	178.6	Thulium	Tm	169.4
Indium	In	114.8	Tin	Sn	118.7
Iodine	I	126.932	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.17
Krypton	Kr	82.9	Vanadium	V	50.96
Lanthanum	La	138.9	Xenon	X	130.2
Lead	Pb	207.2	Ytterbium	Yb	173.6
Lithium	Li	6.94	Yttrium	Y	88.9
Lutecium	Lu	175.0	Zinc	Zn	65.38
Magnesium	Mg	24.32	Zirconium	Zr	91.
Manganese	Mn	54.93			

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PREFACE

The time is, happily, past when "Chemistry for Medical Students," "Quantitative Analysis for Engineers" and similar titles, indicating treatises on the spoon-feeding of special dishes of easy chemical cookery to the classes of persons indicated, met any very general demand on the part of teachers. Even in our highly specialized chemical science of today and in its enormously diversified applications to industrial and economic problems, we recognize the futility of attempting to train students for technical or professional careers by teaching them only the mechanical notions and processes of chemistry without the scientific development of fundamentals.

The authors have tried to keep this idea in view in the compilation of this book. The discussion of special methods (largely "official," wherever applicable) for the analysis of materials of prime importance to chemical students of agricultural materials and of agricultural problems forms an important portion of the book; but we subscribe very heartily to the belief that one of the things most needed by scientific agriculture today is an increasing body of agricultural chemists who understand the importance of desiring to know *why* matters are thus and so.

The introductory course in general quantitative analysis, in Part I, deals with a select list of such analytical processes as may be considered useful for impressing upon the mind of the student the principles of analytical work, as well as the importance of exercising intelligence and care in all work of the laboratory. Bearing in mind the fact that in most college curricula this first course must necessarily be brief, the typical classes of methods for a given determination have been treated together. This, in turn, has involved a preliminary discussion of materials and methods of both gravimetric and volumetric analysis.

Part II, dealing with certain special measurements, has been included in recognition of the fact that the highly important instruments and methods there discussed are too seldom understood by the chemists who use them in industrial work. In our own classes we have found lectures upon the theoretical principles underlying the construction and use of these forms of apparatus to be of very great value.

In Part III is included a treatment of the six classes of materials most often considered in courses in agricultural analysis, and probably of interest to the greatest number of agricultural chemists. The significance of the results of the analyses, in connection with agricultural problems, has been given as much attention as was thought possible, without going outside the proper scope of a book of this character. This, it is believed, will add an interest to the laboratory work and supply a certain motivation, otherwise largely lacking.

In certain parts of the book we have drawn rather freely upon portions of another text by one of us.[1] This is particularly true in the discussion of materials and general operations, of the analysis of oils, fertilizers and dairy products and of the determination of nitrogen. Certain cuts have been borrowed from the same source, while others are from original drawings, made by G. B. Wilson.

Problems in analytical calculations have not been included. Several good problem texts are now available and the authors believe that a systematic course with one of these, as an accompaniment to the laboratory work and lectures, is the best method of impressing this phase of the subject upon the mind of the student.

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[1] MAHIN, "Quantitative Analysis."

INTRODUCTION

For the most part the operations of analytical chemistry fall naturally into quantitative lines. This is particularly true of analysis as applied to agricultural problems because the qualitative composition of most agricultural materials is usually fairly accurately known from the nature and proposed use of the materials themselves.

The qualitative method for the detection of a given element or compound frequently involves the use of the same reactions as those that are fundamental to the quantitative determination of the same materials and in these cases, especially, it is most convenient to modify the details of the experiment so as to make a quantitative determination possible in the beginning, rather than to repeat the work in this manner after the completion of a qualitative analysis. This is not universally true and there will be occasional instances in which the complete qualitative analysis will save the labor of quantitative determination of elements not present in any significant quantity.

As the name implies, quantitative analysis has for its object the determination of the *quantity* (usually, though not always, expressed as per cent) of the various constituents of a material under investigation. The constituents determined may be elements or radicals of a compound, mixture or solution. The particular method to be used for a given material will be chosen according to circumstances and, to some extent, according to individual preference or available equipment. It will necessarily be modified if interfering substances are present. On this account it is desirable first to learn a few methods for the quantitative determination of some common elements in pure compounds and later to apply these and other methods to a more extended analysis of more complicated materials.

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QUANTITATIVE AGRICULTURAL ANALYSIS

PART I

GENERAL ANALYSIS

CHAPTER I

THEORY AND GENERAL PRINCIPLES

Gravimetric Analysis.—When the quantitative composition of a material is learned through the direct application of the analytical balance the method is known as a "gravimetric" one. In principle the method is comparatively simple. A certain quantity of the well mixed sample is weighed accurately. It is then subjected to a series of operations, as a result of which a certain element or radical is finally separated from other constituents, either in its simple form or, as is more often the case, that of a pure compound of known formula. The latter is then weighed accurately. The two weights thus obtained and the known composition of the pure compound provide the necessary data for the calculations.

The determination of phosphorus in a phosphate rock may be taken as an example. The rock may contain ordinary tricalcium phosphate, $Ca_3(PO_4)_2$, as its chief constituent but it will also contain varying quantities of other materials, such as clay, quartz sand, limestone and iron oxide, so that the formula as given above cannot be assumed to be a correct representation of the composition of the material. The latter is therefore carefully sampled and a small portion is accurately weighed. It is then treated with an acid and the insoluble silica and silicates are removed by filtration. All of the phosphorus is then precipitated as ammonium phosphomolybdate, a complex substance represented by the formula $(NH_4)_3PO_4.12MoO_3$. This is filtered out, washed, redissolved and finally precipitated as magnesium ammonium phosphate, $MgNH_4PO_4$, which is washed and then changed to magnesium pyrophosphate, $Mg_2P_2O_7$, by heating strongly in a previously weighed crucible. From the weight of the crucible, with and without the pyrophosphate, the weight of the latter is found.

Factors.—The formula for magnesium pyrophosphate shows that it contains 27.87 per cent of phosphorus $\left(\frac{2P \times 100}{Mg_2P_2O_7} = 27.87\right)$. Multiplying this figure by the weight of pyrophosphate found and dividing the product by the weight of sample gives the per cent of phosphorus in the phosphate rock. Stated as a formula:

$$\frac{2 \times 31.04 \times 100\ W}{222.72\ S} = \text{per cent P in sample,} \qquad (1)$$

where W = grams of magnesium pyrophosphate found and S = grams of sample taken. No matter how many different samples of rock or other material might be subjected to this experimental process, the calculation would always follow the lines indicated in Eq. (1) and, since the only variables in this equation are the weights of sample and of pyrophosphate, the constants may be collected:

$$\frac{2 \times 31.04 \times 100}{222.72} = 27.87 = F. \qquad (2)$$

The quantity F is called a "gravimetric factor" and, since the procedure for phosphorus as already outlined is an illustration of the procedure for all gravimetric determinations, this factor may be calculated once for all for each type of determination and recorded, together with its logarithm, in a convenient place. Equation (1) is then a special application of the more general equation:

$$\frac{F\ W}{S} = x, \qquad (3)$$

F always indicating the per cent of the determined element or combination of elements in the *weighed precipitate*, as calculated from the chemical formula, and x representing the per cent of the same entity in the *sample* analyzed.

As indicated in the preceding paragraph, a combination of elements (as an oxide or radical) may be calculated. For example the factor for phosphorus pentoxide would be

$$\frac{100\ P_2O_5}{Mg_2P_2O_7} = \frac{14208}{222.72} = 63.79.$$

Factor Weights.—In Eq. (3) F is a constant for all determinations of the particular element or group of elements for which it has been calculated. It is possible to choose the weight of the sample taken so as to simplify the calculation of this equation. For instance, by taking a sample weight equal in grams to the value of the factor, $\frac{F}{S}=1$ and Eq. (3) becomes:

$$W=x. \qquad (4)$$

In such a case the weight of precipitate, expressed in grams or fractions, becomes per cent, or fractions, of the constituent determined.

A weight of sample equal in grams to the value of the factor is usually too large a quantity to be handled readily and a definite fraction of this weight (as 0.5, 0.2, 0.1, etc.) may be used instead. Any such weight is called a "factor weight," which may be defined as *a quantity equal in weight units to the value of the gravimetric factor, or to some simple fraction of this factor.*

Continuing the illustration given above, the factor weight of sample actually taken would be, for the sake of convenience, 0.6379 gm, in which case the per cent of phosphorus in the sample would be one hundred times the weight, in grams, of magnesium pyrophosphate found.

When a Factor Weight Should be Used.—In considering the actual practice of the operations with the balance it will be found that the manipulation of the sample to obtain any previously specified quantity requires considerable time, if the weighing is to be done accurately. One cannot judge quantities accurately by means of the eye and it becomes necessary to adjust the sample while it is on the balance pan, very carefully by removing or replacing very minute quantities. On the other hand, it is a comparatively simple matter to take approximately the required quantity and to weigh this accurately, using the figure thus found in later calculations. It may then easily be seen that all of the convenience and time-saving element that is involved in the calculations where factor weights (or, in fact, any other definitely prescribed weights) have been used, may be more than lost in the time and trouble required for adjusting the sample weight to this exact value.

For the reason just mentioned it is inadvisable to use factor weights *except in cases where relatively large amounts of sample* *may be used or where no great accuracy is required.* In such cases the sample weight may be accurately and quickly adjusted to the second or third decimal and the remaining uncertainty will be relatively insignificant. For example, if a 10-gm sample of soil is to be used for a nitrogen determination, an uncertainty of 1 mg in weighing will involve only 0.01 per cent of the total nitrogen found. But if a 0.5-gm sample of limestone were to be used for a determination of calcium, this same uncertainty would amount to 0.2 per cent.

Temperature Systems.—In nearly all scientific work the Centigrade system is used exclusively for indicating temperatures and in this book all temperatures mentioned are in Centigrade *unless otherwise designated.* In some instances the special agricultural analyst will have to use the Fahrenheit system in order to conform to established usage. When this is done in the following pages, the letter "F" will follow the figures indicating the temperature.

Volumetric Analysis.—The final determination of per cent by volumetric methods is not made by means of weighing a precipitate. The balance is generally used, as in gravimetric methods, for weighing the sample. The solution of the latter is then brought into definite reaction with another solution of an appropriate reagent (a **standard solution**) until the reaction is exactly completed. The concentration of the standard solution is accurately known as a result of a previous analysis (a **standardization**) and the volume required is measured accurately by means of a graduated burette. The product of the required volume of the standard solution and its concentration, giving the weight of the dissolved reacting material, serves as a measure of the determined constituent of the sample, just as the weight of the precipitate does in gravimetric analysis, the only difference in principle being the use of the weight of a *reacting* body instead of that of a *containing* body as a measure of the thing to be determined. With this exception the calculations will be similar to those of gravimetric analysis, a **titration** serving instead of a weighing.

As an illustration, the determination of sodium hydroxide in an impure sample may be cited. A weighed quantity of the material is dissolved and titrated by a standard solution of hydrochloric acid, a drop or two of an appropriate indicator, as methyl orange or methyl red, being added to show the end point of the reaction.

If V = cubic centimeters of standard solution required, C = concentration of standard solution (gm of HCl per cc), S = gm of sample used, Eq_{HCl} = equivalent weight (see page 7) of hydrochloric acid (36.468), and Eq_{NaOH} = equivalent weight of sodium hydroxide (40.008), then

$$V\,C = \text{gm HCl used}, \tag{1}$$

$$\frac{V\,C\,Eq_{\mathrm{NaOH}}}{Eq_{\mathrm{HCl}}} = \text{gm NaOH in sample used}, \tag{2}$$

$$\frac{100\,V\,C\,Eq_{\mathrm{NaOH}}}{S\,Eq_{\mathrm{HCl}}} = \text{per cent NaOH in sample.} \tag{3}$$

Of course this derivation is based upon the assumption that sodium hydroxide is the only basic substance present in the sample.

As in gravimetric analysis it is convenient to collect all of the constants of the final expression. For all determinations of sodium hydroxide that are made by means of this particular standard solution of hydrochloric acid, V and S are the only variables. The quantity:

$$\frac{C\,Eq_{\mathrm{NaOH}}}{Eq_{\mathrm{HCl}}} = \frac{40.008\,C}{36.468}$$

may be called the "base factor" of the acid. This can then be simplified and recorded upon the label of the bottle. Let this be designated by F_B. Thereafter, so long as this solution is used for the determination of sodium hydroxide in other samples, the calculation of the results of titrations will be made by means of the equation:

$$\frac{100\,V\,F_B}{S} = \text{per cent NaOH.} \tag{4}$$

If the same standard solution is to be used for the determination of any other base it will be necessary to recalculate the value for F_B for this substance and to use the new value in an equation similar to Eq. (4). If a new standard solution of a different concentration is prepared, or if the concentration of the original standard has changed, a new value for F_B is calculated.

Adjustment of Sample Weight.—The volumetric calculations already explained have been made upon the assumption that the sample weight was not adjusted to any particular value although it was, of course, accurately determined. In Eq. (4) F_B is a constant for this particular standard solution in this particular determination. Therefore if some care is exercised in adjusting the sample weight, S, so that it will bear some simple relation to F_B, the calculations will be materially simplified. For example, if S is made to equal 100 F_B, Eq. (4) will become:

$$V = \text{per cent NaOH.} \tag{5}$$

That is, each cubic centimeter of standard solution used in the titration represents a weight of sodium hydroxide which is 1 per cent of the sample weight, so that the burette reading becomes a percentage reading. From this the rule follows:

To make the burette reading a direct percentage reading, use a sample weight equal to 100 F_B.

In practice it often happens that such an adjustment calls for a too small weight of sample and it does not then provide for sufficient accuracy. Ten or one hundred times this weight is often taken, making 1 cc of standard solution indicate tenths or hundredths of 1 per cent.

Use of Aliquot Parts.—If the adjustment of sample weight must be made with a high degree of accuracy it may be that the extra time involved in the adjustment will not be compensated by time saved in calculations, in which case such adjustment will not be desirable. But if relatively large samples may be used for the analysis an error in weighing becomes of proportionately less importance and adjustment may be made more rapidly and less carefully. These considerations apply as in gravimetric analysis (page 4).

The use of large samples is rendered practicable by the use of the principle of aliquot parts. Some simple multiple of the required weight is taken and the solution is diluted to a definite volume in a volumetric flask and well mixed. A definite fraction of this solution is taken for the analysis and the proper factor to correct for this is used in the calculation of results. For example, if a degree of accuracy carried to the fourth decimal place is required in weighing 0.3943 gm for a single analysis, ten times