An introduction to analytical chemistry

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An Introduction to Analytical Chemistry

Product Code No. 57017

Published in Great Britain in 1973 by BDH Chemicals Ltd Poole BH12 4NN and printed by Dawson & Goodall Ltd., The Mendip Press, Bath

FOREWORD

A good basic knowledge of analytical chemistry procedures can be considered as being essential for most laboratory technicians irrespective of the type of laboratory work on which they are engaged. Many young men and women entering the chemical industry straight from school neither have the necessary practical experience nor sufficient theoretical background and most Companies find it necessary to give these young entrants some form of intensive training course. In fact the Chemical and Allied Industries Training Board emphasises that such a course is essential and have produced outlines of suitable programmes. Courses developed in this way usually consist of practical laboratory work to familiarise the assistant with the processes and raw materials used and products manufactured by the particular Company. They generally have a bias towards analytical chemistry since this discipline is most adaptable to meet the training needs. Unfortunately such practical based courses often provide only a very sketchy treatment of the theoretical aspects of the work.

This book is written by a Chemist with a sound industrial background and based upon many years' experience of training young laboratory technicians. It combines a description of simple laboratory techniques and experiments with a sound theoretical backing at the right level for the young intake and as such fills a real gap in their training needs. I have no doubt that it will serve a most useful purpose in supplying the supplementary reading for technicians during their apprenticeship and will provide a useful book of reference to back up their subsequent general laboratory work.

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PREFACE

This book was written originally for the benefit of GCE 'O' and 'A' level new entrants to the Analytical Department of BDH Chemicals Ltd. to be read during their initial training period. The purpose was to provide some basic theoretical background to the analytical methods which they were practising.

Having extended and refined the text, the author hopes that others will also find it useful, for example sixth formers preparing for GCE 'A' level Chemistry.

There has been no attempt to deal in depth with the various topics, the idea being to give the essential basic principles of a wide range of analytical techniques and to present, as it were, a summary of analytical chemistry as a whole. The individual subjects may be pursued in greater detail by reference to standard text-books and a small selection of examples for further reading is given in the bibliography.

The author hopes that the book will be easy to read and readily understood. In most industrial laboratories the day-to-day matters of practice and administration generally occupy the whole of the working day and sometimes more besides. On the occasion when one is able to refresh ones basic knowledge, it is useful to have at hand a set of condensed notes in which a large area can be scanned in a short time. In this sense it is hoped that the book will be of value to the more senior analyst from time to time.

The author would like to thank Professor T. S. West of Imperial College of Science and Technology and Mr. G. B. Thackray, B.Sc., M.Chem.A., F.R.I.C., Public Analyst for the City of Portsmouth who very kindly read the first draft and offered some valuable suggestions; also Mr. C. Whalley, B.Sc., F.R.I.C., President of the Analytical Division, Chemical Society, for writing the Foreword.

G. F. LEWIS
April 1973

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1. INTRODUCTION AND SOME STATISTICAL CONCEPTS

Analytical chemistry is concerned with the identification of unknown materials, the identification of impurities, measurements of physical constants, and the quantitative determination of purity and impurities. It may involve the examination of solids, liquids or gases, and the whole range of complexity of materials from very pure single chemicals to complex mixtures and natural products such as ores and crude petroleum. The first operation in a quantitative analysis is the preparation of a *laboratory sample* truly representative of the bulk material. This may be a simple matter if the material is a well-mixed liquid in a single container or an elaborate procedure in the case of, say, a shipload of zinc blende.

The quantitative analysis continues with the measurement of the analytical sample by weighing on a balance or by measuring its volume in volumetric glassware such as a pipette. The object is then to process and/or manipulate the sample in such a way that the major component or impurity being determined may be accurately and precisely measured and related to the original sample quantity. The result may be expressed as a percentage, as a weight per unit volume or as parts per million.

It is important to appreciate that both from a practical and a philosophical point of view it is *impossible to determine the absolute truth* about the composition of a material. The analysis is always the best possible attempt to *estimate* the required value. It is also important to realise that a single analysis on a single sample cannot give any information at all regarding the *average purity* or *average impurity* level, *uniformity of purity* or the *distribution of impurity levels* throughout the bulk. To estimate these values, *a series of replicate samples* must be taken from different parts of the batch and preferably analysed independently. It will then be possible to talk with qualified precision about these variable factors.

Here are the more important terms used in the discussion of analytical results:

Accuracy: The closeness of agreement between the experimental and the true value.

Precision: The closeness of agreement between replicate experimental values. Good *repeatability* and *reproducibility* means high precision, but this does not necessarily mean high accuracy because the method may have a *systematic error*.

Repeatability: The closeness of agreement between replicate determinations on the *same* sample by the *same* analyst, using the *same* reagents.

Reproducibility: The closeness of agreement between replicate determinations on *different* samples of the same substance, by *different* analysts.

Error: A divergence from the truth from *inherent* causes in the usual procedure.

Mistake: A divergence from the truth arising from *unintentional* departure from the usual procedure.

Systematic Error or Bias: A persistent error not eliminated by averaging.

Random Error: Individually unpredictable, but *averaging zero* over a long series.

Mean: The *average* of a series of similar determinations. These may have been carried out under conditions of 'repeatability' or under the conditions of 'reproducibility'. It is given the symbol $\bar{x}$, relating to a series of individual results x.

Variance: A measure of the dispersion of replicate results around their *mean*. It is given the symbol, s^2 for reasons which will become apparent below.

If the mean $= \bar{x}$, and $S(x) =$ sum of the individual results x, and $n =$ number of results in the series:

$$\text{Then } \bar{x} = \frac{S(x)}{n}$$

The individual error will be $(x - \bar{x})$, and the variance is defined as:

$$s^2 = \frac{S(x - \bar{x})^2}{n - 1} = \frac{\text{sum of the squares of the individual errors}}{\text{total no. of results} - 1}$$

Standard Deviation

$$s = \sqrt{\text{variance}}$$

Example: The calculation of the standard deviation of a series of ten analytical results.

Individual Results x	*Error* $x - \bar{x}$	*Squares* $(x - \bar{x})^2$
10·51	−0·10	0·0100
10·57	−0·04	0·0016
10·60	−0·01	0·0001
10·63	+0·02	0·0004
10·59	−0·02	0·0004
10·62	+0·01	0·0001
10·61	0·00	0·0000
10·68	+0·07	0·0049
10·63	+0·02	0·0004
10·61	0·00	0·0000
Mean $\bar{x} = 10{\cdot}61$		0·0179 = sum of squares of errors $S(x - \bar{x})^2$

$$\therefore \text{ Variance } s^2 = \frac{0{\cdot}0179}{9} = 0{\cdot}002$$

$$\therefore \text{ Standard Deviation } s = \sqrt{0{\cdot}002} = 0{\cdot}045$$

Quicker methods are available for calculating Standard Deviation, but the classical method illustrates the relationships between the several parameters.

Having estimated the Standard Deviation for a particular analytical procedure certain estimates may be made concerning a single estimation and a series of replicate results. It is important to note that the Standard Deviation value calculated from replicate results by the same analyst on the same sample (conditions of repeatability) will be smaller than the value calculated from replicate results by different analysts on different samples (conditions of reproducibility). The latter value is the true Standard Deviation of the procedure.

The Normal Error Curve (See Fig. 1)

If a large series of analyses is carried out the results will always fall within the area enclosed by the normal error curve provided that the conditions for carrying out the analysis have not varied within the series. The total area enclosed by the curve represents 100% of the results and the percentage fractional area between any two limits on the horizontal axis indicates the percentage of results which may be expected to occur between these limits.

e.g. The area shaded ////// represents 66% of the whole which means that 66% of the results of a series of replicates may be expected to be within the limits $\bar{x} \pm s$. If we add to this the area shaded \\\\\\ the total shaded area represents 95% of the whole which means that 95% of the results may be expected to be within the limits $\bar{x} \pm 2s$. Finally if we include the area shaded ∴∵∴ we find that over 99% of the results will be within the limits $\bar{x} \pm 3s$, where in each case $\bar{x}$ = the mean of all the results and s = the standard deviation.

Calculations

In analytical calculations, it is common to work out the results to three significant figures.

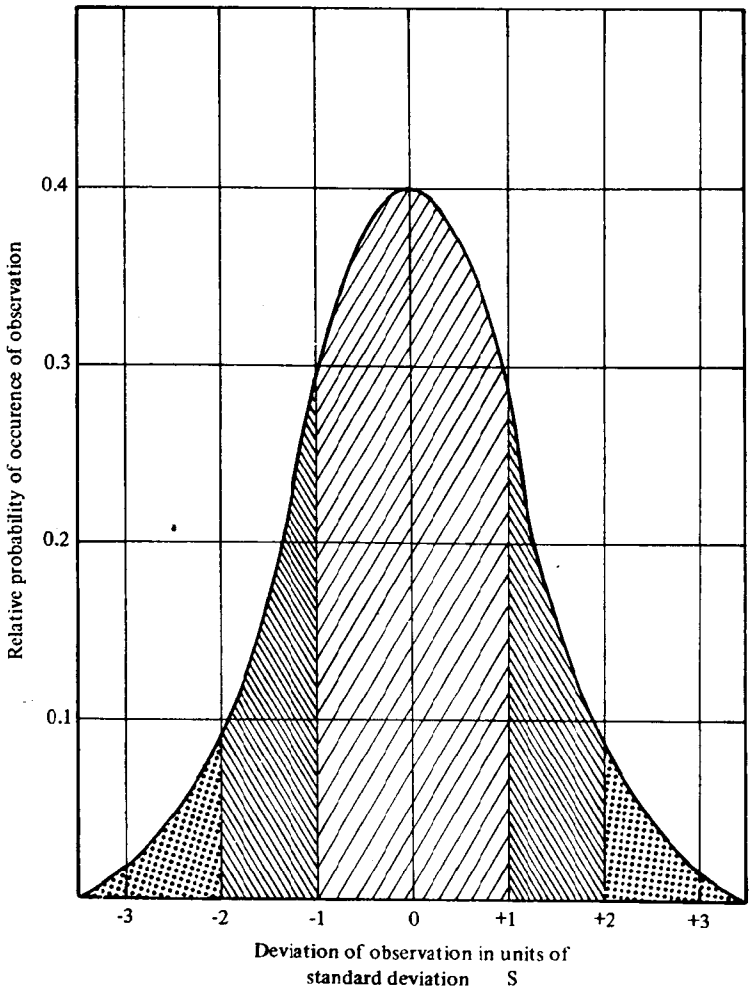
Four figure log tables are quite satisfactory for this purpose but when a large number of calculations have to be made, the procedure is tedious and open to error in transferring the readings from the tables to the paper on which the addition or subtraction is being made.

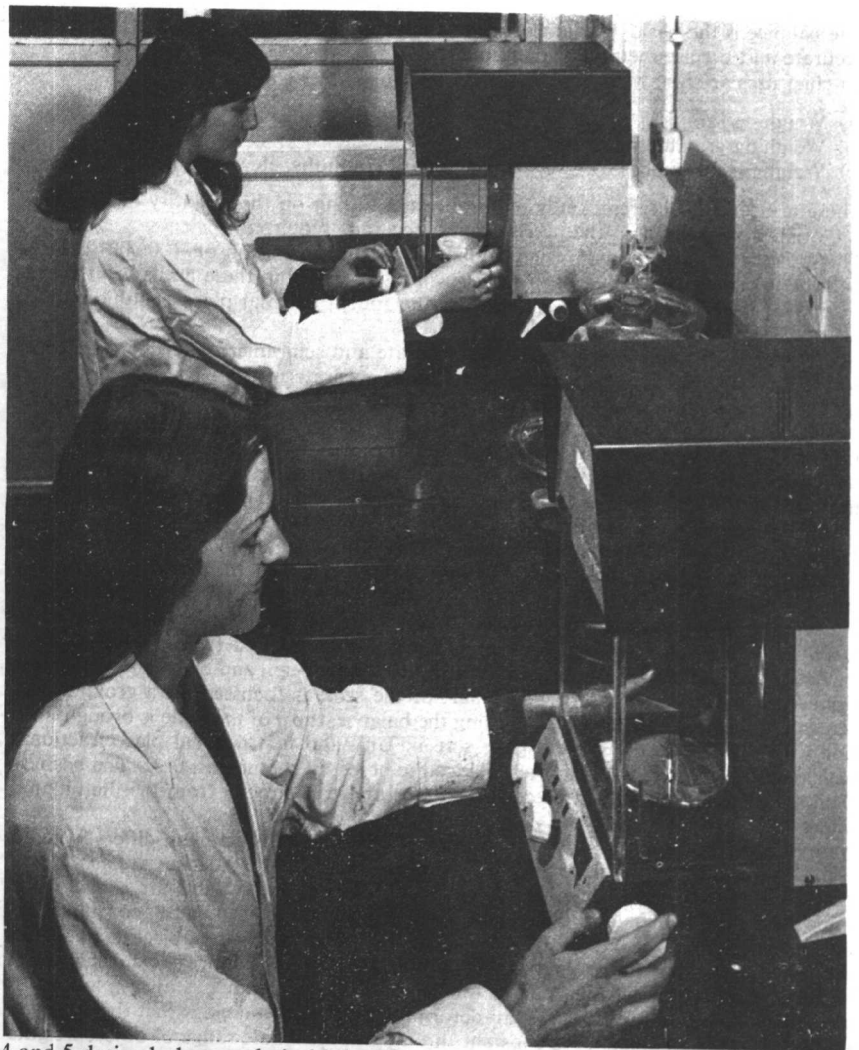
An ordinary slide rule is only satisfactory for rough calculations since the fourth significant figure can be estimated only at the lower end of the scale and even the third place is not accurate at the higher end.

A Fuller Calculator is equivalent to a slide rule many yards long and the scale is accommodated by being wound spirally round a cylinder. It is used in a very similar way to an ordinary slide rule and gives four figures throughout the entire scale.

Nowadays many laboratories are equipped with mechanical or electronic calculating machines which are capable of handling calculations involving many significant figures. It is important to remember that if the precision of the analytical method justifies reporting the result to 'x' significant figures, the calculation should be made to 'x + 1' significant figures. This applies whichever method is used.

fig 1 The normal error curve





4 and 5 decimal place analytical balances

2. THE BALANCE

The balance is the basic instrument of the analytical laboratory and is by far the most accurate and precise method of measurement.
Its chief uses are for:

(a) Weighing samples
(b) Weighing gravimetric precipitates
(c) Weighing substances for preparing standard solutions, etc.

There are several different kinds of balance depending on the quantity of substance it is wished to weigh and the precision and accuracy required.
The most common type will weigh up to 200 g with a precision of $\pm$ 0·0001g. If the balance is properly adjusted its accuracy will also fall within these limits. This means that *three decimal places are accurate* but the fourth decimal place is subject to an inherent error of $\pm$ 1.
There are *rough balances* which are less accurate and semi-micro and micro balances which are ten times and a hundred times more accurate respectively. The latter will weigh to an accuracy and precision of $\pm$ 0·00001g for a semi-micro balance and $\pm$ 0·000001g for a micro balance.
Earlier balances were free swinging, but modern analytical balances are of the *direct reading type*, in which the beam *comes to rest* somewhere between the extremes of its motion and the weight is read directly. This is achieved by the use of damping cylinders acting on each end of the beam.
Usually the larger fractional weights and often unit weights are placed on the beam by means of a dial-operated system of levers and this removes the necessity of handling small weights. Different makes of balance differ in the way in which the final weight is obtained. A common system is for the total swing of the balance to correspond to a weight difference of 0·1000g. A calibrated graticule numbered from 0 $\rightarrow$ 1000 is attached to the end of a lever attached to the centre of the beam and by means of a simple optical system, the image of a small part of the scale is focussed on a ground glass screen carrying a single line. Before using the balance, the 0 of the scale is brought into line with the line of the ground glass screen. Unit and first decimal place fractional weights are placed on the beam to balance the object to the nearest 0·1g. The beam is then released and the last three decimal places are read directly from the illuminated scale.
Many balances are constant load instruments. This type of instrument differs from an ordinary balance in the following way. An empty ordinary balance is *unloaded* on both sides of the beam. The object is placed on the pan and weights are *added* to the opposite end of the beam to balance the weight of the object. An empty constant load balance carries a 200g weight at each end of the beam. When the object is placed on the pan, weights are *removed* from this end of the beam to balance the constant load of 200g attached to the other end of the beam. Thus the balance is always loaded to the same extent and there is constant deformation. The advantage is that the accuracy and precision of the balance is constant throughout the whole range of object weights from 0 $\rightarrow$ 200g. With an ordinary balance, the accuracy and precision deteriorates

with increasing load. The knife edges and planes of a constant load balance are made of a specially tough material which readily withstands the strain of a 200g constant load.

Balances are delicate and expensive instruments and must always be handled with great care.

Chemicals must never be placed directly on the pans or else serious corrosion of the metal will occur.

No object must be placed on the pan unless it is at the temperature of the balance room or else serious errors may occur and the balance may even be permanently damaged.

3 SAMPLING

The sample submitted to the analytical laboratory for chemical or physical tests must be *absolutely representative of the bulk material*, otherwise the results will be misleading or even useless, and thoughtful and skilful laboratory work will have been carried out in vain. Quite often some preliminary measurements are required, such as particle size estimation or bulk density.

Mention was made in Section 1 of the impossibility of deducing average purity or average impurity levels from a single analysis of a single sample taken from the bulk material. In fact it is very occasionally permissible to make such deductions, for example if it is wished to examine a small scale preparation of a liquid or solution, which is known to be single phase and homogeneous from its mode of preparation. Even here one has to be careful, especially in the case of a liquid mixture prepared from components of widely differing specific gravities or in the case of an aqueous solution which requires a further adjustment of solute to achieve the correct concentration. It is quite remarkable how difficult it is to produce a perfectly homogeneous composition in such circumstances even when all the constituents are liquids and the system is single phase.

In general, *sampling difficulties increase with the size of the bulk of the material* and the extent of its subdivision, and it is frequently necessary to devise quite elaborate procedures. Since each case needs to be considered on its own merits it will be possible to mention only general principles.

Liquids are generally sampled with a *dip tube or sampling pipette* made of glass, polythene or stainless steel, of a size suitable for the type of container encountered. For *solids* the commonest device is a *sampling spear*, which is a hollow tube suitably shaped so that it may be inserted deep into the bulk of the material for the withdrawal of a sample. Gases well above atmospheric pressure may be reduced to just above atmospheric pressure by means of reducing valves and then passed through a container until all the air is displaced when the container is sealed. A sample may be withdrawn for analysis by displacing the gas with a suitable inert liquid.

When dealing with multi container batches of heterogeneous solid materials it is frequently necessary to have a section of personnel specially equipped and trained in sampling techniques in order to produce authentic laboratory samples. In the classic method successive equal increments are taken from the bulk and blended to produce the *gross sample*. The number and size of these increments will depend on the nature of the material, and the number of containers. The gross sample is ground to a certain particle size and mixed. The material is laid out on a flat surface in the form of a circular pile of uniform depth, quartered, and opposite quarters are discarded. The remainder is further reduced and mixed and the quartering is repeated, again discarding opposite quarters. Eventually the gross sample is reduced to a size suitable for submitting to the analytical laboratory and of sufficiently small particle size to ensure homogeneity of composition between replicate weighed analytical samples. The smaller the *analytical sample*, the more finely divided should be the *laboratory sample*. Today equipment is available for carrying out this reduction automatically and the *rotary divider* may be mentioned.

Special care needs to be taken to prevent changes in the laboratory sample between its preparation and the chemical or physical analysis. For example, hygroscopic materials must be adequately protected from the atmosphere and should be analysed as soon as possible after the sample has been received in the laboratory.

4 PRELIMINARY TREATMENT OF THE ANALYTICAL SAMPLE

In most cases a series of operations will have to be carried out on the analytical sample before a final measurement may be made, and in general the more complex the material, the more elaborate will be the preliminary treatment. In the case of high purity chemicals, it may be necessary only to dissolve the analytical sample in a suitable solvent, such as water, or dilute aqueous acid, but even here, many substances, because of their sparing solubility in the common solvents, will need special treatment. In the case of more complex materials, the separation of interfering substances may be necessary, involving perhaps the precipitation of the wanted or unwanted substance, or preferential extraction of one or the other into one of the phases of a two-phase liquid system. The object of the preliminary treatment is to convert the analytical sample by chemical or physical means to a state in which the desired constituent may be determined without interference from other constituents. This will involve producing a *solution* containing the *whole of the desired constituent*, in a form which lends itself to determination by one of the techniques described in the later sections of this book. Among the common preliminary procedures may be mentioned the following well-known examples.

Treatment of a sparingly soluble inorganic material

A digestion with nitric acid, hydrochloric acid or aqua regia (1 volume of nitric acid + 2 → 3 volumes of hydrochloric acid) will often be successful in producing a solution of the desired component. With complex ores and silicates, part of the material, in particular the silica, will not pass into solution. A very useful acid solvent is 72% perchloric acid, particularly for some alloy steels, by means of which all but silica is taken into solution, the latter being converted into an easily filterable precipitate. Chromium is converted quantitatively to chromium (VI) and may be determined with particular ease.

A fusion of the sample in a platinum crucible with potassium pyrosulphate is especially useful with certain kinds of ores, particularly rutile, or crude titanium dioxide. This amounts to a powerful acid attack at high temperature. The solid melt is dissolved in water or dilute acid.

Solution may often be brought about by fusing the sample in a platinum crucible with anhydrous sodium carbonate or fusion mixture (an equimolar mixture of sodium and potassium carbonates). On leaching out the melt with water, insoluble carbonates of the more basic metals may be separated from soluble sodium salts of elements which form anions, such as aluminium, and silicon. The carbonates may be dissolved in dilute acid and the analysis continued for the separated groups of elements.

Treatment of organic compounds prior to determination of halogens, sulphur and phosphorus

In recent years, the oxygen flask technique has become widely used. A small sample of 20–30 mg weight is wrapped in a square of paper, or alternatively is placed in a gelatine capsule. It is then placed in a platinum basket suspended from a stopper and is ignited in a closed flask filled with oxygen and containing a small volume of dilute

alkali. The combustion products, carbon dioxide, water, possibly oxides of nitrogen, hydrogen halides and oxides of sulphur and phosphorus are absorbed in the aqueous alkali. Sometimes a few drops of hydrogen peroxide are added to ensure complete oxidation of sulphur compounds to sulphate and phosphorus compounds to phosphate. The resultant halide, sulphate or phosphate is then determined by a standard titrimetric or absorptiometric procedure.

Oxidation of basically organic materials prior to determination of inorganic constituents

It is usual to digest the analytical sample with hot, concentrated sulphuric acid, often in a long-neck (Kjeldahl) round-bottom flask. Eventually, all the organic matter is oxidised and we are left with a sulphuric acid solution of the inorganic constituents. The process may be hastened by the dropwise addition of nitric acid to the hot mixture. In some circumstances, perchloric acid may be used in conjunction with nitric acid, but perchloric acid must never be used alone or if strong reducing agents are known to be present, and in any case it should be used only in conditions which have been proved to be safe. In no circumstances whatever should it be used to digest material whose composition is entirely unknown. Another similar technique is to use a combination of hydrogen peroxide and sulphuric acid.

A wet digestion is preferable to a dry ashing technique because there is less chance of losing certain metals by evaporation of relatively volatile compounds, such as halides of iron (III). If the substance sought does not form volatile compounds it is permissible to ignite the sample in a platinum dish, and by gradually increasing the temperature to about 900°C, to completely oxidise the organic portion of the sample in this way. The inorganic residue may be dissolved in a suitable acid solvent, or fused with sodium carbonate and the analysis continued.

The separation of metals from each other with organic reagents

Many metals ions form complex compounds with certain classes of organic compounds. The first two pre-requisites of the organic compound are that (a) it shall have a replaceable hydrogen ion, i.e. it shall possess an acidic function and (b) it shall have in its molecule an atom with an unbonded pair of electrons; this is often a nitrogen or an oxygen atom.

The simplest organic compound which fulfils these requirements is amino-acetic acid or glycine, $NH_2.CH_2.COOH$, which may be written like this: