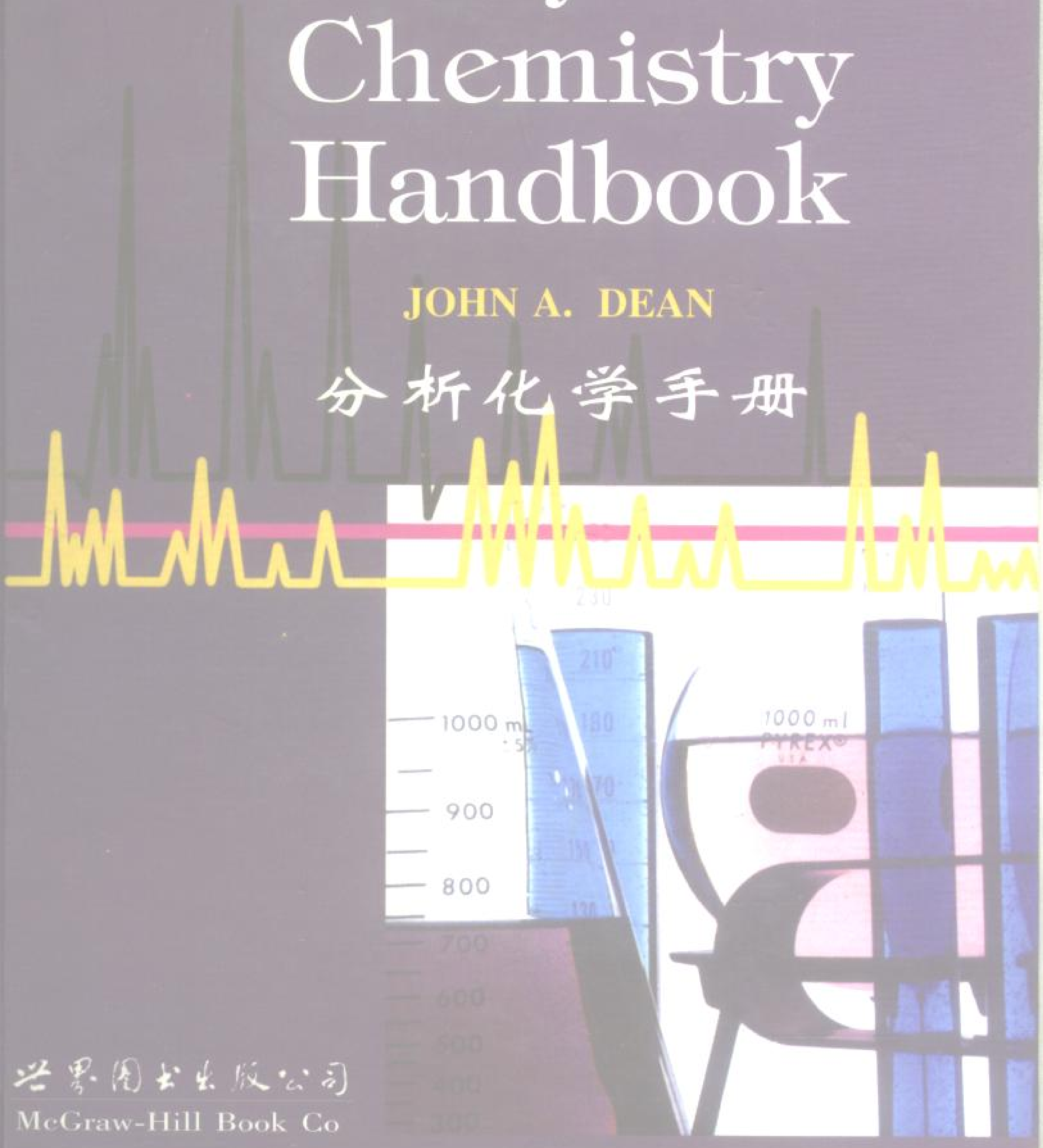
Analytical Chemistry Handbook

JOHN A. DEAN

分析化学手册



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ANALYTICAL CHEMISTRY HANDBOOK

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PREFACE

The growth of modern technology has confronted the analytical chemist with a host of new and increasingly complex materials, has called on that person to provide information about constituents previously unrecognized or ignored, and has posed more stringent demands for greater sensitivity, reliability, and speed. On the other hand, developments in instrumentation and the research of colleagues in allied fields have provided the analyst with new techniques, instruments, procedures, and reagents for dealing with these problems.

This very expansion of equipment, reagents, and methodology has, however, greatly complicated the task of the chemist searching for the best way of attacking a new or unfamiliar sample. This handbook is intended to provide analytical chemists and their colleagues in related sciences with concise and convenient summaries of the fundamental data and the practical procedures that are most important and most useful among the conventional wet and instrumental methods in modern analytical chemistry. All this is presented in a convenient desk-size guide.

Without ready access to the data that describe the behaviors of the various substances present toward different techniques, it is all too easy for the special peculiarity of the one most suitable technique to escape notice. One of the hardest problems in analytical work is in choosing the right technique to solve a problem. With this handbook the reader will have a handy reference all in one place for analytical techniques. The handbook should be especially helpful in those laboratories which may not have developed a wide variety of in-house analytical methods.

Extensive application tables contain just enough information to enable a reader to reach a judgement call about the possible applicability and range or sensitivity of a method plus references that will supply more detailed directions and discussion of the method. Intercomparison of techniques within a general topical area or between one or several topical areas are provided to enable the user to reach a decision on choice of a method. Factors entering into this decision might be cost, time of analysis, sensitivity, reproducibility, and expertise required of the operator. As an aid to understanding the parameters involved in a technique, many examples involving mathematical expressions have been worked out. Illustrative worked examples and troubleshooting sections are included.

Sample preparation prior to analysis is a major analytical challenge; the book expounds the various techniques for extracting analytes from complex matrices and gives approaches to method development. The opening section on preliminary operations of analysis encompasses the important topics of sampling, mixing and sample reduction, moisture and drying, and methods for dissolving the sample. More than likely a preliminary separation will be necessary, perhaps to concentrate the analyte or to remove interference, or both. Preliminary separation methods take the reader through complex formation, masking and demasking reactions, extraction methods, ion-exchange methods, volatilization methods, and conclude with carrier coprecipitation and chemical reduction methods.

Traditional material in the realm of gravimetric and volumetric analysis constitutes the third section. Here are discussed inorganic gravimetric analysis, acid-base titrations in aqueous media and in nonaqueous media, precipitation titrations, oxidation-reduction titrations, and complexometric titrations. The remainder of the book treats the individual areas of instrumental analysis and a selected group of applications. A final section contains information of a general nature.

Although there is no specific section on methods for the analysis of technical materials, the Index is expanded to include references to specific elements or functional groups, and to types of sample matrices, that are tabulated in the many tables within the various sections of the handbook. This style eliminates unnecessary duplication of material.

In all probability, the technique for analyzing the sample for the components requested will require searching through several possible sections of the handbook for an appropriate method. Perhaps a second method will be selected to provide confirmation of the analyte concentration, a method that might be longer or more costly but one not to be used routinely. This collection of information in one book instead of having to make many referrals will assist the reader in selecting the best method(s) for a particular situation. With quick and easy access to the myriad of analytical techniques that the book provides, the reader can either choose the best one or get specific information on the method selected. Only in exceptional cases are procedures described in full. Enough information is provided to enable the user to make a judicious and rational choice from among the techniques and procedure available. Conditions and details of the final measurement are included to serve as a convenient ready reference. References given will direct the user to additional information.

Finally, as results of analyses have been accumulated, some of the statistical treatments outlined in Sec. 20 would be utilized; certainly if a calibration curve is to be prepared, the least square method for the best-fit line should be used and evaluated.

Theoretical discussions have been limited since several excellent texts devoted to instrumental methods (including one coauthored by this editor) are on the market. Likewise, the descriptions of apparatus and methodology are restricted, yet sufficiently comprehensive, to enable the user to judge intelligently between available choices.

The editor would be grateful for suggestions as to organization and scope of the handbook, and for bringing any errors to his attention.

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Grateful acknowledgment is hereby made of an indebtedness to those who contributed to the edited work of Louis Meites, *Handbook of Analytical Chemistry*, and whose compilations continue in use in this handbook.

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SECTION 1

PRELIMINARY OPERATIONS OF ANALYSIS

1.1 SAMPLING

1.1.1 Handling the Sample in the Laboratory

Each sample should be completely identified, tagged, or labeled so that no question as to its origin or source can arise. Some of the information that may be on the sample is as follows:

1. The number of the sample.
2. The notebook experiment-identification number.
3. The date and time of day the sample was received.
4. The origin of the sample and cross-reference number.
5. The (approximate) weight or volume of the sample.

6. The identifying code of the container.
7. What is to be done with the sample, what determinations are to be made, or what analysis is desired?

A computerized laboratory data management system is the solution for these problems. Information as to samples expected, tests to be performed, people and instruments to be used, calculations to be performed, and results required are entered and stored directly in such a system. The raw experimental data from all tests can be collected by the computer automatically or can be entered manually. Status reports as to the tests completed, work in progress, priority work lists, statistical trends, and so on are always available automatically on schedule and on demand.

1.1.2 Sampling Methodology

The sampling of the material that is to be analyzed is almost always a matter of importance, and not infrequently it is a more important operation than the analysis itself. The object is to get a representative sample for the determination that is to be made. This is not the place to enter into a discussion on the selection of the bulk sample from its original site, be it quarry, rock face, stockpile, production line, and so on. This problem has been outlined elsewhere.[1-5] In practice, one of the prime factors that tends to govern the bulk sampling method used is that of cost. It cannot be too strongly stressed that a determination is only as good as the sample preparation that precedes it. The gross sample of the lot being analyzed is supposed to be a miniature replica in composition and in particle-size distribution. If it does not truly represent the entire lot, all further work to reduce it to a suitable laboratory size and all laboratory procedures are a waste of time. The methods of sampling must necessarily vary considerably and are of all degrees of complexity.

No perfectly general treatment of the theory of sampling is possible. The technique of sampling varies according to the substance being analyzed and its physical characteristics. The methods of sampling commercially important materials are generally very well prescribed by various societies interested in the particular material involved, in particular, the factual material in the multivolume publications of the American Society for Testing Materials, now known simply as ASTM, its former acronym. These procedures are the result of extensive experience and exhaustive tests and are generally so definite as to leave little to individual judgment. Lacking a known method, the analyst can do pretty well by keeping in mind the general principles and the chief sources of trouble, as discussed subsequently.

If moisture in the original material is to be determined, a separate sample must usually be taken.

1.1.2.1 Basic Sampling Rules. No perfectly general treatment of the theory of sampling is possible. The technique of sampling varies according to the substance being analyzed and its physical characteristics. The methods of sampling commercially important materials are generally very well prescribed by various societies interested in the particular material involved: water and sewage by the American Public Health Association, metallurgical products, petroleum, and materials of construction by the ASTM, road building materials by the American Association of State Highway Officials, agricultural materials by the Association of Official Analytical Chemists (AOAC), and so on.

A large sample is usually obtained, which must then be reduced to a laboratory sample. The size of the sample must be adequate, depending upon what is being measured, the type of measurement

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[1] G. M. Brown, in *Methods in Geochemistry*, A. A. Smales and L. R. Wager, eds., Interscience, New York, 1960, p. 4.

[2] D. J. Ottley, *Min. Miner. Eng.* 2:390 (1966).

[3] C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Elsevier, London, 1960; Vol. 1A, p. 36.

[4] C. A. Bicking, "Principles and Methods of Sampling," Chap. 6, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, eds., Part 1, Vol. 1, 2d ed., Wiley-Interscience, New York, 1978; pp. 299–359.

[5] G. M. Brown, in *Methods in Geochemistry*, A. A. Smales and L. R. Wager, eds., Interscience, New York, 1960, p. 4.

being made, and the level of contaminants. Even starting with a well-gathered sample, errors can occur in two distinct ways. First, errors in splitting the sample can result in bias with concentration of one or more of the components in either the laboratory sample or the discard material. Second, the process of attrition used in reducing particle sizes will almost certainly create contamination of the sample. By disregarding experimental errors, analytical results obtained from a sample of n items will be distributed about μ with a standard deviation

$$s = \frac{\sigma}{\sqrt{n}} \tag{1.1}$$

In general, σ and μ are not known, but s can be used as an estimate of σ, and the average of analytical results as an estimate of μ. The number of samples is made as small as compatible with the desired accuracy.

If a standard deviation of 0.5% is assigned as a goal for the sampling process, and data obtained from previous manufacturing lots indicate a value for s that is 2.0%, then the latter serves as an estimate of σ. By substituting in Eq. (1.1),

$$0.5 = \frac{2.0}{\sqrt{n}} \tag{1.2}$$

and $n = 16$, the number of samples that should be selected in a random manner from the total sample submitted.

To include the effect of analytical error on the sampling problem requires the use of variances. The variance of the analysis is added to the variance of the sampling step. Assuming that the analytical method has a standard deviation of 1.0%, then

$$s^2 = \frac{(\sigma_s^2 + \sigma_a^2)}{\sqrt{n}} \tag{1.3}$$

where the numerator represents the variance of the sampling step plus the variance of the analysis. Thus

$$(0.5)^2 = \frac{[(2.0)^2 + (1.0)^2]}{n} \tag{1.4}$$

and $n = 20$, the number of samples required. The above discussion is a rather simple treatment of the problem of sampling.

1.1.2.2 Sampling Gases.[6] Instruments today are uniquely qualified or disqualified by the Environmental Protection Agency. For a large number of chemical species there are as yet no approved methods.

The size of the gross sample required for gases can be relatively small because any inhomogeneity occurs at the molecular level. Relatively small samples contain tremendous quantities of molecules. The major problem is that the sample must be representative of the entire lot. This requires the taking of samples with a "sample thief" at various locations of the lot, and then combining the various samples into one gross sample.

Gas samples are collected in tubes [250 to 1000 milliliter (mL) capacity] that have stopcocks at both ends. The tubes are either evacuated or filled with water, or a syringe bulb attachment may be

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[6] J. P. Lodge, Jr., ed., *Methods of Air Sampling and Analysis*, 3d ed., Lewis, Chelsea, Michigan, 1989. Manual of methods adopted by an intersociety committee.

used to displace the air in the bottle by the sample. For sampling by the static method, the sampling bottle is evacuated and then filled with the gas from the source being sampled, perhaps a cylinder. These steps are repeated a number of times to obtain the desired sampling accuracy. For sampling by the dynamic method, the gas is allowed to flow through the sampling container at a slow, steady rate. The container is flushed out and the gas reaches equilibrium with the walls of the sampling lines and container with respect to moisture. When equilibrium has been reached, the stopcocks on the sampling container are closed—the exit end first followed by the entrance end. The sampling of flowing gases must be made by a device that will give the correct proportion of the gases in each annular increment.

Glass containers are excellent for inert gases such as oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide. Stainless-steel containers and plastic bags are also suitable for the collection of inert gases. Entry into the bags is by a fitting sealed in and connected to the bag to form an integral part of the bag. Reactive gases, such as hydrogen sulfide, oxides of nitrogen, and sulfur dioxide, are not recommended for direct collection and storage. However, Tedlar™ bags are especially resistant to wall losses for many reactive gases.

In most cases of atmospheric sampling, large volumes of air are passed through the sampling apparatus. Solids are removed by filters; liquids and gases are either adsorbed or reacted with liquids or solids in the sampling apparatus. A flowmeter or other device determines the total volume of air that is represented by the collected sample. A manual pump that delivers a definite volume of air with each stroke is used in some sampling devices.

1.1.2.3 Sampling Liquids. For *bottle sampling* a suitable glass bottle of about 1-L capacity, with a 1.9-centimeter (cm) opening fitted with a stopper, is suspended by clean cotton twine and weighted with a 560-gram (g) lead or steel weight. The stopper is fitted with another length of twine. At the appropriate level or position, the stopper is removed with a sharp jerk and the bottle permitted to fill completely before raising. A cap is applied to the sample bottle after the sample is withdrawn.

In *thief sampling* a thief of proprietary design is used to obtain samples from within about 1.25 cm of the tank bottom. When a projecting stem strikes the bottom, the thief opens and the sample enters at the bottom of the unit and air is expelled from the top. The valves close automatically as the thief is withdrawn. A *core thief* is lowered to the bottom with valves open to allow flushing of the interior. The valves shut as the thief hits the tank bottom.

When liquids are pumped through pipes, a number of samples can be collected at various times and combined to provide the gross sample. Care should be taken that the samples represent a constant fraction of the total amount pumped and that all portions of the pumped liquid are sampled.

Liquid solutions can be sampled relatively easily provided that the material can be mixed thoroughly by means of agitators or mixing paddles. Homogeneity should never be assumed. After adequate mixing, samples can be taken from the top and bottom and combined into one sample that is thoroughly mixed again; from this the final sample is taken for analysis.

For sampling liquids in drums, carboys, or bottles, an open-ended tube of sufficient length to reach within 3 mm of the bottom of the container and of sufficient diameter to contain from 0.5 to 1.0 L may be used. For separate samples at selected levels, insert the tube with a thumb over the top end until the desired level is reached. The top hole is covered with a thumb upon withdrawing the tube. Alternatively the sample may be pumped into a sample container.

Specially designed sampling syringes are used to sample microquantities of air-sensitive materials.

For suspended solids, zone sampling is very important. A proprietary zone sampler is advantageous. When liquids are pumped through pipes, a number of samples can be collected at various times and combined to provide the gross sample. Take care that the samples represent a constant fraction of the total amount pumped and that all portions of the pumped liquid are sampled.

1.1.2.4 ***Sampling Compact Solids.*** In sampling solids particle size introduces a variable. The *size/weight ratio b* can be used as a criterion of sample size. This ratio is expressed as

$$b = \frac{\text{weight of largest particle} \times 100}{\text{weight of sample}} \tag{1.5}$$

A value of 0.2 is suggested for b; however, for economy and accuracy in sampling, the value of b should be determined by experiment.

The task of obtaining a representative sample from nonhomogeneous solids requires that one proceeds as follows. A gross sample is taken. The gross sample must be at least 1000 pounds (lb) if the pieces are greater than 1 inch (in) (2.54 cm), and must be subdivided to 0.75 in (1.90 cm) before reduction to 500 lb (227 kg), to 0.5 in (1.27 cm) before reduction to 250 lb (113 kg), and so on, down to the 15-lb (6.8-kg) sample, which is sent to the laboratory. Mechanical sampling machines are used extensively because they are more accurate and faster than hand-sampling methods described below. One type removes part of a moving stream of material all of the time. A second type diverts all of the stream of material at regular intervals.

For natural deposits or semisoft solids in barrels, cases, bags, or cake form, an auger sampler of post-hole digger is turned into the material and then pulled straight out. Core drilling is done with special equipment; the driving head should be of hardened steel and the barrel should be at least 46 cm long. Diamond drilling is the most effective way to take trivial samples of large rock masses.

For bales, boxes, and similar containers, a split-tube thief is used. The thief is a tube with a slot running the entire length of the tube and sharpened to a cutting edge. The tube is inserted into the center of the container with sufficient rotation to cut a core of the material.

For sampling from conveyors or chutes, a hand scoop is used to take a cross-sectional sample of material while in motion. A gravity-flow auger consists of a rotating slotted tube in a flowing mass. The material is carried out of the tube by a worm screw.

1.1.2.5 ***Sampling Metals.*** Metals can be sampled by drilling the piece to be sampled at regular intervals from all sides, being certain that each drill hole extends beyond the halfway point. Additional samples can be obtained by sawing through the metal and collecting the "sawdust." Surface chips alone will not be representative of the entire mass of a metallic material because of differences in the melting points of the constituents. This operation should be carried out dry whenever possible. If lubrication is necessary, wash the sample carefully with benzene and ether to remove oil and grease.

For molten metals the sample is withdrawn into a glass holder by a sample gun. When the sample cools, the glass is broken to obtain the sample. In another design the sampler is constructed of two concentric slotted brass tubes that are inserted into a molten or powdered mass. The outer tube is rotated to secure a representative solid core.

1.2 MIXING AND REDUCTION OF SAMPLE VOLUME

1.2.1 Introduction

The sample is first crushed to a reasonable size and a portion is taken by quartering or similar procedures. The selected portion is then crushed to a somewhat smaller size and again divided. The operations are repeated until a sample is obtained that is large enough for the analyses to be made but not so large as to cause needless work in its final preparation. This final portion must be crushed to a size that will minimize errors in sampling at the balance yet is fine enough for the dissolution method that is contemplated.

Every individual sample presents different problems in regard to splitting the sample and grinding or crushing the sample. If the sample is homogeneous and hard, the splitting procedure will present

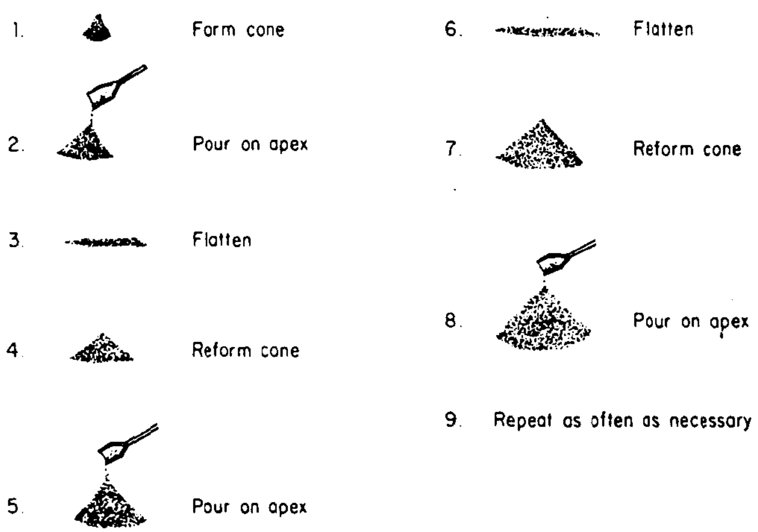

FIGURE 1.1 Coning samples. (*From Shugar and Dean,* The Chemist's Ready Reference Handbook, *McGraw-Hill, 1990.*)

no problems but grinding will be difficult. If the sample is heterogeneous and soft, grinding will be easy but care will be required in splitting. When the sample is heterogeneous both in composition and hardness, the interactions between the problems of splitting and grinding can be formidable.

Splitting is normally performed before grinding in order to minimize the amount of material that has to be ground to the final size that is suitable for subsequent analysis.

1.2.2 Coning and Quartering

A good general method for mixing involves pouring the sample through a splitter repeatedly, combining the two halves each time by pouring them into a cone.

When sampling very large lots, a representative sample can be obtained by coning (Fig. 1.1) and quartering (Fig. 1.2). The first sample is formed into a cone, and the next sample is poured onto the apex of the cone. The result is then mixed and flattened, and a new cone is formed. As each successive sample is added to the re-formed cone, the total is mixed thoroughly and a new cone is formed prior to the addition of another sample.

After all the samples have been mixed by coning, the mass is flattened and a circular layer of material is formed. This circular layer is then quartered and the alternate quarters are discarded. This process can be repeated as often as desired until a sample size suitable for analysis is obtained.

The method is easy to apply when the sample is received as a mixture of small, equal-sized particles. Samples with a wide range of particle sizes present more difficulties, especially if the large, intermediate, and small particles have appreciably different compositions. It may be necessary to crush the whole sample before splitting to ensure accurate splitting. When a coarse-sized material is mixed with a fine powder of greatly different chemical composition, the situation demands fine grinding of a much greater quantity than is normal, even the whole bulk sample in many cases.

FIGURE 1.2 Quartering samples. The cone is flattened, opposite quarters are selected, and the other two quarters are discarded. (*From Shugar and Dean, 1990.*)

TABLE 1.1 Sample Reduction Equipment

Sample composition	Hardness, mohs	Cutting mill	Jaw crusher	Cross beater mill	Rotor beater mill	Centrifugal grinder	Mortar mill	Mixer mill	Ball mills	Micro rapid mill
Basalt, carbide, carborundum, cement clinker, corundum, diabase, glass, granite, iron alloys, iron ore, quartz	Very hard and brittle, 6.5–8.5	☐	■	☐	☐	☐	■	■	■	■
Artificial fertilizers, ash, calcite, feldspar, hematite, magnetite, marble, sandstones, slags	Hard, 4.5–6.5	☐	■	☐	☐	☐	■	■	■	■
Barite, bauxite, calcite, dolomite, gneiss, kaolin, limestone, magnetite, pumice, stones	Medium hard, 2.5–4.5	☐	■	■	■	■	■	■	■	■
Graphite, gypsum, hard lignite, mica, salts, talc	Soft, 1.5–2.5	☐	■	■	■	■	■	■	■	■
Cardboard, cereals, feeds, fish, food, dried fruit, leather scraps, paper, plant material, textiles	Fibrous and cellulose type	■	☐	☐	☐	■	☐	■	☐	☐
Duroplastic and thermoplastic materials, artificial resins, rubber	Elastic	■	☐	☐	☐	■	☐	■	☐	☐
Maximum sample size, cm^3		< 500	< 300	< 300	< 300	10–500	10–150	< 10	< 10	10–300
Initial particle size, mm		4–80	< 150	< 20	< 20	< 10	< 8	< 6	< 6	< 8
Final particle size, μm		< 150	< 100	70	70	40	35	< 35	< 10	< 10

■, Suitable; ☐, not suitable.

Data supplied by Brinkmann Instruments, Inc.