U. S. DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS

STANDARD SAMPLES

GENERAL INFORMATION

CIRCULAR OF THE BUREAU OF STANDARDS, No. 398

U. S. DEPARTMENT OF COMMERCE
R. P. LAMONT, Secretary
BUREAU OF STANDARDS
GEORGE K. BURGESS, Director

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I. INTRODUCTION

In the past 30 years analytical chemistry has taken a place of such importance in many manufacturing industries that the analyst not only is called upon to determine the policy of the works in buying raw material and in grading finished products, but often his figures are required at every step of the process. This has necessitated

many changes and advances in this branch of the science of chemistry, for on the one hand the great chemical complexity of many industrial products has increased the difficulty of securing good determinations and on the other hand it has been necessary to obtain results much more promptly than heretofore.

Hence a need has arisen for special aids by which the ends named can be reached with the minimum expenditure of time.

Other aids, not involving analytical operations, are needed for the grading of many materials. These needs can be met, often by the employment of special substances of accurately determined composition, or which, without knowledge of their exact composition, are suitable for a special purpose. Such substances are termed standards for the particular end they are to serve.

II. FUNCTION OF STANDARD SAMPLES

1. ANALYZED SAMPLES

The variable factors in analytical chemistry are many. The purity of reagents used, the influence of other elements on the determination of a particular element, the influence of temperature, changes of concentration, solubility of precipitates, catalytic phenomena recognized and unrecognized, solubility of glass vessels, etc.—these are but a few of the long list with which the chemist has to contend. It is obvious that the technical chemist, when called upon to devise new and rapid methods to fit complex materials of a hitherto uninvestigated nature, can not generally avail himself of the methods of the research chemist in handling but one or two of these variables at a time. The time at his disposal for investigation is necessarily limited, and research must be conducted along lines of greatest efficiency. The result has been the evolution of the standard analyzed sample. This may be defined as a material resembling as closely as possible in chemical and physical nature the material with which the chemist expects to deal, and which has been analyzed by a sufficient number of methods and analysts to establish its average composition with considerable certainty. The use of such a sample is quite obvious where the chemist has at hand a material which, when subjected to the usual operation of analysis, will behave like the stock material he expects to analyze. Errors arising from solubility of precipitates, varying concentrations, effects of one element upon the precipitation of another, etc., will affect both sample and standard alike. Hence, if standard and sample are analyzed at the same time (and under practically identical conditions) and results are obtained for the standard corresponding to those obtained by the other analysts, the presumption is strong that the figures obtained for the unknown material are equally accurate, whereas wide divergence from the determinations made by the other chemists on the standard sample shows at once something radically wrong, such as improper methods, faulty manipulation, or impure reagents. Thus, in the simplest possible manner and in the shortest possible time a large number of variable factors have been simultaneously investigated with almost the same result as though each had been taken up separately.

2. SAMPLES OF GREAT PURITY

For many purposes substances of fixed and definite chemical composition are required. These may be chemical elements or compounds, each of the highest attainable purity. Being pure, they have a fixed and definite composition. They find use as standards for volumetric analysis, for calibrating calorimetric bombs, polarimeters, thermometers, pyrometers, and other instruments.

3. OTHER SAMPLES

Closely related to pure metals are metallic alloys of definite composition and free from all other elements than those which it is desired to have present. Still other samples owe their value to the possession of certain definite physical properties. Such, for example, are materials graded according to fineness of grain and intended for sieving and other tests.

III. HISTORY OF THE BUREAU OF STANDARDS' SAMPLES

When the chemistry division of the Bureau of Standards was organized it was but natural that it should sooner or later be confronted with this requirement of the industries of the country. In 1905 the American Foundrymen's Association turned over to the bureau its standardized pig-iron samples, comprising four sets and covering a considerable range of compositions. The distribution of these was carried on after they had been reanalyzed by the bureau chemists and by some commercial testing laboratories. The bureau, however, had not participated long as a distributor of these irons before it was realized from the numerous inquiries received that the preparation of new materials for the steel trade was in order, and consequently, aided by valuable suggestions and advice from various steel companies and from A. L. Colby, at that time a member of the visiting committee of the bureau, and others, the issuing of various kinds of steel samples was begun and is being actively continued at the present time. In 1905 the committees of the American Chemical Society upon uniformity of technical analysis, and upon zinc-ore analysis, assigned their samples to the Bureau of Standards for distribution. Along with the demand for steel and iron products there has developed demand for other alloys, for ores, and numerous other products, which is also being met as fast as the facilities of the bureau permit.

IV. CHOICE OF STANDARD MATERIALS

1. METALS AND ALLOYS

(*a*) *Standards for analysis.*—Theoretically, there should be provided for the chemist at a works as many standard samples as he has different kinds of materials to deal with. Thus, in a steel works making steel by the Bessemer, basic open-hearth, and crucible processes, in addition to standards for all the raw materials, there should be as many steel standards as there are processes, and a standard sample for each different composition produced by the same

process if there is much range. Sometimes, however, there need not be absolute similarity in all respects between the product and standard; for instance, sometimes a steel sample is ordered on the basis of its carbon content without very much regard to the percentage of phosphorus present. This is a matter that must be determined, however, for each individual case, and no general rule can be given. The bureau, in determining the question as to the composition of samples to be issued, is guided by the number and kind of requests received and by the advice of those engaged in the industries interested.

Metal samples intended as checks on analysis should be in grains of small and uniform size, so that attack by chemical reagents is comparatively rapid. It is especially important to have uniformity of size and freedom from dust, for it is only in this way that it is possible to obtain and maintain a perfect mixture. The works, in preparing raw materials for analyzed samples, must see that they possess extraordinary homogeneity. This is secured by casting, forging, heat treatment, rolling, etc., under expert supervision. In general, the greatest homogeneity is possible with metals whose constituents form solid solutions. Wherever eutectics separate there is danger of segregation, which can be avoided only by the greatest care throughout subsequent operations. In the course of preparing the chips by machining of various kinds the particles of the samples must not be heated by the tool so much as to cause superficial oxidation, nor must they be exposed to the danger of corrosion by moist air after their preparation.

(*b*) *Samples for physical measurements.*—If a pure substance is to be used as a means of defining some physical constant, such as heat of combustion or melting point, the material chosen should be stable and such that it may be obtained in a pure state or readily purifiable by further treatment. The physical constant defined by use of the material should be of a useful magnitude. For example, of combustion samples one having about the same heat of combustion as the average coal usually would be preferred. It is also desirable that the physical constant should be accurately defined by the material, so that results obtained will not be sensibly affected by slight variations in procedure; and finally, it is desirable that the physical property should be only slightly affected by impurities in the material.

2. ORES AND SIMILAR MATERIALS

(*a*) *Ores.*—The ideal ore sample is one which is practically a chemically pure compound of the type which is being smelted, usually an oxide or a sulphide. Occasionally ores are found in nature which satisfy this condition. If an ore sample is a blend, the difficulty of uniform mixing is a prominent one, and where it is a question of the most thorough mixing of 200 or 500 pounds of such a blend under conditions of chemical cleanliness the problem is very complex. Another desirable quality in an ore is permanency with regard to its hygroscopic condition, the hardest of all to meet. In the case of ores containing 60 or 70 per cent of the metal which is to be recovered by smelting, differences of a few tenths of a per cent of moisture make very serious differences in the percentage found.

A fine state of divison is even more important here than in the case of metals, owing to the oftentimes difficult solubility, but this leads to difficulties, for the readiness with which moisture is taken up by powdered materials is a function of their fineness. Hence not all ores are suitable as analytical standards, but the defect of varying moisture content becomes less the lower the content of the important constituent. It is especially undesirable that the mineral components of an ore should differ markedly in density; for, if they do, segregation after mixing is inevitable.

(*b*) *Ceramic materials.*—Standard samples of ceramic materials must not undergo a permanent change as a result of exposure to ordinary atmospheric conditions. Raw materials, such as limestones, dolomites, and feldspars, do not combine with water or carbon dioxide, and so samples for analysis can be reproduced by drying at 105° to 110° C. On the other hand, certain calcined materials, such as soda-lime glass or burnt magnesite, form compounds that can not be broken up by heating at moderate temperatures. Analyses of standard samples of such materials are computed on the basis of "loss on ignition" instead of "dried at 105° to 110° C.," provided the samples for analysis can be reproduced by reasonable care in igniting the sample.

(*c*) *Cement.*—In many industries a control of the fineness of pulverized materials is essential, and woven-wired sieves are commonly used for this purpose. Sieves having as many as 325 wires to the linear inch are now regularly manufactured. The Bureau of Standards has adopted specifications for a series of testing sieves.

In the cement industry the No. 200 sieve is the one most used. Since cement of normal manufacture, which has been carefully dried, mixed, and stored in hermetically sealed jars, will maintain its original state of subdivision without appreciable change, samples of this material have been prepared for use as a part of the testing of No. 200 sieves at the bureau. As a matter of routine testing, this fineness determination is carried out only for all full-height No. 200 sieves. The result of this test is a correction to each sieve tested with respect to the standard cement sample. The sieving correction thus determined would apply to other materials, the particles of which are similar to those of cement, but the correction factors would not at all apply for materials differing considerably in shape from cement particles. These samples of cement are furnished by the bureau at a nominal price in order that users of No. 200 sieves, who desire to make their own standardization tests, may do so.

The cement samples are furnished in two degrees of fineness, one a normally ground cement of which approximately 78 per cent passes the No. 200 sieve, the other a more finely ground cement of which approximately 88 per cent passes the No. 200 sieve.

V. PREPARATION OF MATERIALS

1. METALS AND ALLOYS

(*a*) *Standards for analysis.*—The raw material for the steel samples is supplied in the form of round bars about 5 inches in diameter, which have been carefully rolled or forged. These are cut into convenient lengths in the shop, and, in order to see whether they

are sufficiently homogeneous, samples taken by drilling at intervals across the ends of the bars are analyzed for carbon. If these preliminary tests show the bars to be sufficiently uniform, they are turned into chips of the desired form. The amount of sample prepared in the past has ranged from 300 to 1,000 pounds. Sometimes it is not possible to produce directly on the lathe exactly the form of chip desired, and it then becomes necessary to grind the material in order to break up clumps of chips. The process of preparing the metals as outlined is somewhat wasteful both of time and material, but so far as steel is concerned it seems the only practicable one at present. Of course, in the preparation of these samples it is necessary to take the utmost precautions to prevent contamination by oil, dust, etc., and the storage of the finished samples requires similar precautions.

Pig-iron samples must be carefully prepared. Chips are cut from hollow cylinders, 22 inches in length and 12 inches in outside diameter, with walls about 3 inches in thickness. The castings are usually bottom-poured in greensand. Particles of free graphite, which separate during the machining operation, can not be mixed uniformly with the particles of iron, and hence cause difficulty in obtaining a homogeneous sample for analysis. Another fact which must be considered is that the carbon contents of the different sized particles of iron will vary. It is, therefore, essential that the chips be of uniform size. In preparing the bureau's standard samples of cast iron the machined sample is first sieved to remove the fine particles of iron and free graphite. It is then mixed in a special machine, through which a strong current of air is passed for the purpose of removing any free graphite that is still present. The mixing gives rise to a certain amount of fine material through crushing, and the mixed sample is therefore again sieved to obtain the standard sample, which is that portion which passes a No. 14 and remains on a No. 35 sieve.

A sample of rolled brass has been prepared by clamping together in a vise a number of sheets of the material, averaging about one-hundredth of an inch in thickness, and cutting chips from these with a milling cutter. This method can not be employed for steel and iron samples, owing to the oxidation of the surfaces of rolled sheets and to the limitation of composition thus imposed.

The preparation of other nonferrous alloys presented many obstacles, owing to the fact that it was difficult to obtain homogeneous castings. Chips obtained from such castings required subsequent thorough mixing, which resulted in discoloration caused chiefly by oxidation.

Samples of cast bronze (88–8–2–2), lead-base bearing metal (80–10–10), and tin-base bearing metal (89–7.5–3.5) have, however, been prepared. The bronze was chill cast in 1 by 12 by 24 inch slabs under the supervision of P. E. McKinney at the Naval Gun Factory, Washington, D. C., and subsequently machined at this bureau. As the slabs were remarkably uniform in composition, no mixing of the chips was necessary. The samples of lead-base and tin-base bearing metals were prepared under the supervision of W. A. Cowan at the National Lead Co., Brooklyn, N. Y. Both were obtained as fine particles of 40 to 200 mesh size by " atomizing " the

molten metal with hot dry air. The bearing metal samples are remarkably homogeneous and free from oxide.

(*b*) *Samples for physical measurements.*—Metals and alloys especially intended for checking physical properties do not, as a rule, need to be reduced to small particles like the analytical standards. Their mode of preparation varies with the nature of the material. Commercial materials, usually of high quality, serve as the starting point and are refined in a variety of ways—such as by electrolytic deposition or distillation, followed in some instances by appropriate casting.[1]

2. ORES, CEMENTS, ETC., GRINDING, AND MIXING

Ores and similar materials are prepared with comparative ease by grinding in a pebble mill lined with enameled brick and supplied with flint or porcelain pebbles.

With such mills a subsequent sifting of the powder is imperative, for the balls chip (particularly those of flint) and the chips produced in the latter stage of grinding are not reduced to powder. In general, the grinding of ores in contact with iron or steel surfaces is objectionable, sometimes quite inadmissible, for it always results in the incorporation of considerable amounts of metallic particles with the sample, and these are especially objectionable in that they are never uniformly distributed. Unfortunately the sifting above referred to occasions more or less segregation, hence thorough remixing must supervene under conditions that will permit no entrance of foreign matter. This thorough mixing applies to irons and steels as well as to ores and cements. Mixers, each built of two hollow, internally enameled, cast-iron cones, bolted together at their bases and turning about a hollow axle at right angles to their common axis, have been devised at the bureau and are used for mixing metal samples. A blast of air may be directed through the axle if desired.

3. STORING, BOTTLING, AND ANALYSIS OF FINE-GRAINED SAMPLES

The mixed samples are transferred to numbered large containers and from these to the small bottles in which they are to be finally distributed. Before the final bottling, samples for analysis are re-removed from the jars and sent, one each, to a number of analysts. In general, three types of analysts are chosen—commercial chemists, works chemists, and chemists of the bureau. When all the analytical results have been received they are inspected, and, if not sufficiently concordant, analysts are sometimes requested to repeat the determinations without knowing in which direction from the average their value lies.

4. PURE CHEMICALS

In the selection of pure chemicals which may serve as primary standards for various purposes the effort has been made to choose stable substances of the highest purity that can be obtained at a reasonable expense. So far as possible, the impurities in the final

[1] For more detailed description of the preparation of these samples see Bureau of Standards Circular 66, Standard Samples for Thermometric Fixed Points. This circular costs 5 cents, and can be obtained from the Superintendent of Documents, Washington, D. C.

products are reduced to such an amount as to be outside the present limits of experimental error of the method which it is intended to standardize; that is, the materials may be considered entirely pure for the purposes under consideration. In addition, however, careful tests are made to detect and if possible determine quantitatively any impurities present in order that corrections may be made if necessary. Thus far the following samples of pure chemicals have been issued:

(*a*) *Sucrose.*—Calorimetric and saccharimetric standard: The raw material for the standard sucrose samples is drawn from the purest granulated sugar of commerce. A comparatively dilute solution is filtered and boiled in an improved vacuum apparatus to high concentration at temperatures below 35° C. Minute crystals form under the influence of constant stirring and are separated by a centrifugal machine. The process is repeated until analysis shows a negligible amount of ash and reducing substances. The final crystals are ground in an agate mortar and dried in a vacuum over lime. The substance is only slightly hygroscopic but should be kept tightly stoppered in a dry compartment, at a temperature not much above 20° C., in order to prevent a slight spontaneous decomposition. Standard sucrose samples prepared by a modified alcohol-precipitation method may also be obtained.

(*b*) *Dextrose.*—Standard reducing sugar: In the preparation of this material the purest dextrose or "corn sugar" of commerce is dissolved by heating in 40 per cent of its weight of water, treated with decolorizing carbon, and filtered. The filtered solution, which is water-white, is placed in a rotating crystallizer and allowed to crystallize in motion. The crystals are centrifuged and washed with alcohol. The entire process is repeated until a satisfactory purity is attained. The crystals obtained in this fashion contain one molecule of water of crystallization, but the substance loses this at 60° C., a temperature considerably below the melting point. The remaining traces of moisture are removed by exposing to a temperature of 70° C. for short time. The dried substance, in spite of its finely divided condition, is not very hygroscopic, but should be kept in a desiccator.

The normal weight (that is, the weight required to give a rotation on the quartz wedge saccharimeter equivalent to 26 g of sucrose in 100 cc) is 32.231 g. The specific rotation for wave length 5461 *A* is represented by the following formula:

$$\left[\alpha\right]_{5461\ A}^{20.0^\circ\ \mathrm{C.}} = 62.032 + 0.0422xp + 0.0001897\ p^2$$

where p is the percentage by weight in vacuo.

(*c*) *Benzoic acid.*—Issued primarily as a calorimetric standard, but may also be employed in acidimetry: Benzoic acid, as purchased in the open market, may contain chlorine or sulphur compounds if made synthetically, or gums and related organic acids if made from natural sources. The original standard sample made at the bureau was prepared from the purest synthetic acid obtainable, by two crystallizations from ethyl alcohol, followed by one crystallization from water and fractional sublimation in vacuum.[2] Experience at

[2] George W. Morey, J. Am. Chem. Soc., vol. 34, p. 1027, 1912.

this bureau has indicated that this elaborate purification is unnecessary if the purest commercial product is used. The raw material used must analyze 99.9 per cent benzoic acid and be free from chlorine and sulphur compounds. When this material is crystallized once from water and subjected to fractional sublimation in a vacuum, a product which is equivalent to the original standard is obtained. The progress of purification is followed by titration with standard alkali, which under the above conditions is the most delicate test of the purity of the acid. Benzoic acid is neither appreciably volatile nor hygroscopic [3] and, when kept in stoppered bottles, can be used for all but the most accurate work without preliminary drying.

For details regarding the use of combustion samples, consult Bureau of Standards Circular No. 11.

(*d*) *Sodium oxalate.*—Issued primarily as an oxidimetric standard, but may be used for acidimetry: This material was prepared, upon rigid specifications, by the Mallinckrodt Chemical Works, St. Louis, Mo., and was carefully tested at this bureau. For details regarding the use of sodium oxalate, consult Bureau of Standards Circular No. 40 on Sodium Oxalate as a Standard in Volumetric Analysis.

(*e*) *Naphthalene.*—Calorimetric standard: As commercial naphthalene is made from coal tar, the impurities possibly present are numerous. Some of these are very difficult to remove and hard to detect. The bureau purchases the purest product obtainable from commercial sources and, in testing the material, is guided largely by the melting point, sulphur content, and action of the sample toward sulphuric acid. The present sample, No. 38b, was specially prepared by the Eastman Kodak Co., Rochester, N. Y. Naphthalene is not hygroscopic but is appreciably volatile, and for this reason care must be taken to prevent error in accurate work.

(*f*) *Potassium acid phthalate.*—Issued primarily as an acidimetric standard: This material was prepared by the Mallinckrodt Chemical Works, St. Louis, Mo., and was carefully tested at this bureau.

(*g*) *Arsenic trioxide.*—Issued primarily as an iodometric standard: This sample was prepared by the Mallinckrodt Chemical Works, St. Louis, Mo., and was carefully tested at this bureau.

VI. USES OF THE STANDARD SAMPLES

The principal uses of the bureau's analyzed samples appear to be as follows:

First. In the settling and avoiding of disputes between buyers and sellers. Such disputes very frequently arise through the selection of inappropriate or faulty methods of analysis by one of the chemists, and the analysis of a standard material usually brings these to light before the case comes to court.

Second. In standardizing calorimeters for gas and coal tests and polarimeters for sugar tests.

Third. In standardizing pyrometers for use in the annealing of steels, alloy steels, and other metallurgical products.

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[3] It has been found, however, to take up moisture from the air very slowly. Old samples may contain as much as 0.1 per cent of water, which can be easily removed by careful fusion. See "Note on the use of benzoic acid as a standard material," by E. R. Weaver, in J. Am. Chem. Soc., vol. 35, p. 1309, 1913.

Fourth. For checking the sieving values of sieves employed in the cement industry.

Fifth. In checking methods of analysis and in standardizing solutions used by analysts.

Sixth. In investigating improved and more rapid methods of analysis.

Seventh. In research work in educational institutions.

VII. GENERAL CONSIDERATIONS

In conclusion, it may be said that the bureau's work in providing analyzed and other samples has attracted considerable attention and interest, partly because of its intrinsic merit and partly because the bureau has sought, through brief mention in the leading chemical and engineering journals of the country, to secure the attention and interest of those who need this kind of service. The result has been the hearty and oftentimes unsolicited cooperation of some of the leading technical societies of the country. Among these are the American Foundrymen's Association, the American Brass Founders' Association, the American Steel Manufacturers' Association, the United States Steel Corporation, the American Chemical Society, the Institute of Metals, the Portland Cement Association, the American Society of Civil Engineers, and the American Society for Testing Materials. Some of these organizations have committees on which the bureau is represented. It is one of the functions of these committees, which include in their personnel members of the technical staffs of some of the leading manufacturers of the country, to suggest some of the future lines of activity of the bureau in its work on standard samples and to aid in selecting and securing the necessary raw materials.

VIII. STANDARD SAMPLES ISSUED OR IN PREPARATION

A separate leaflet, entitled "Supplement to Bureau of Standards Circular No. 398," contains a complete list of samples available at the given date, together with analyses, physical constants, weights, and fees. This circular will be sent upon request.

IX. ORDERING AND SHIPPING REGULATIONS

1. ORDERING

Orders should give both the number and name of the sample wanted. Example: No. 9c Steel, Bessemer, 0.2 C. The list of standard samples, their numbers, prices, and analyses are to be found in the "Supplement to Bureau of Standards Circular No. 398." No samples of sizes other than those listed are distributed.

2. TERMS AND SHIPPING

(*a*) *Domestic.*—Samples may be paid for in advance with order. If a remittance does not accompany the order, all samples will be sent under Government frank by parcel post C. O. D. in the United States and its possessions. It is therefore important that firms with

branch laboratories send remittances with their orders if the laboratories can not receive C. O. D. packages. Both the central office and branch laboratory will be notified when shipment is made. No discounts are allowed on any orders.

(*b*) *Foreign.*—All foreign shipments require prepayment. With the exception of Mexico and Canada, 30 cents postage must be added for every 300 g of sample. Shipments intended for Mexico and Canada will be sent under Government frank, but not C. O. D.

(*c*) *Money orders, etc.*, should be payable to the Bureau of Standards.

3. BOTTLING

Iron, steel, and ore samples are sent in screw-capped glass bottles, and organic samples in glass-stoppered bottles under seal.

4. LITERATURE

Detailed certificates of analysis are sent under separate cover to the same destination as the samples. These certificates give the results obtained by all of the analysts for all of the constituents determined by them. Gummed labels, with the summary of analysis, are also furnished with most samples. Circulars containing information on certain samples may be obtained upon request. In the case of new or renewed samples provisional typewritten certificates are supplied until they can be replaced by the printed certificates and labels when ready.

5. SAMPLES OUT OF STOCK

The preparation of "renewal" samples is intended to be complete at the time each kind of sample becomes exhausted, but, owing to delays encountered in obtaining a proper grade of material and for other reasons, this is not always possible. If orders are received for samples that are out of stock, notice will be mailed to that effect. Notice will also be sent when the "renewal" is ready. The "renewal" of an analyzed sample will have a composition more or less different from that of its predecessor, but, as regards the characteristic constituent or constituents, will pattern after it closely.

6. NEW SAMPLES

When new samples are issued announcement will be made in scientific and trade journals.

7. MIXING

In order to overcome the effect of any segregation of granular samples in shipment the contents of each bottle (except the pure chemicals) *should be thoroughly mixed before any is used for analysis.*

GEORGE K. BURGESS,
Director.

Approved:
E. F. MORGAN,
Acting Secretary of Commerce.

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