TEACHING ANALYSIS

THE subject matter and manner of presentation of analysis to students in our colleges have been static for many years. Teaching analysis often has been justified because of the principles taught. Certainly no other chemistry course is justified on this basis. The recent symposium held at Chicago on contents of the beginning course on quantitative analysis, sponsored by the Divisions of Analytical and Micro Chemistry and Chemical Education, reveals that considerable thought is being given to the problem, and that old-time lethargy is being replaced by a dynamic approach to the means by which modern analysis can be integrated into the subject matter of analytical courses. The enthusiasm of a zealot of modern analysis will not be satisfied with the proposed changes, which to him seem inadequate, but every subject always receives too little attention according to the partisan viewpoint of specialists. The encouraging thing is that the problem is recognized, and an attempt is being made to solve it.

It is rightly recognized that an analyst cannot be developed by taking one or two courses, and that most of those taking the subject never intend to become analysts. Some old-line teachers fail to see this, and the degree of excellence in the course is therefore sometimes judged solely by how close a student comes to the correct answer. This insistence causes many students to develop a dislike for analysis, especially if they do not intend to become specialists. It is therefore all the more important to acquaint them with what analysis is and by what techniques the answer is obtained. The perfection in techniques is unimportant in the first course, although a knowledge of the degree of perfection that may be obtained by experts and those specializing in the subject should be imparted. The course in analysis is usually the student's first approach to the scientific method used in research, and it is highly important, therefore, that he appreciate the reasons behind the rigorous impersonal integrity required.

Rather than deal only with time-honored methods of filtration, separation, etc., would it not be more interesting to have the student use one of these techniques in experiments and to cover by demonstration or lecture the other methods that can be used? In this way the student will come to realize the scope of the field, the bare essentials of which he is just learning in his first course.

In schools with large classes it is possible to give courses to meet the requirements of particular groups. We believe that some attempt should be made in all courses to teach that it is on the basis of the physical and chemical properties of compounds that methods have been and will be devised. It is the intelligent selection, interpretation, and application of these properties that form the basis of analytical chemistry. If this is made clear to the student, analytical procedures will better fit into his basic scientific thinking and training.

On several fundamental points there was surprising agreement in the symposium discussion. It was felt that the first course should stress tidiness and neatness, and familiarize the student with the potentialities of application of analytical methods. The chemical engineering student should be indoctrinated with a philosophy of quantitative analysis and given a thorough understanding of its usefulness in the laboratory, so that he will be equipped to take the subject out of the laboratory and know how it may be used in the plant. The importance of being able to select the proper variable for analysis and the value of instrumental methods should be stressed.

It is beginning to be realized that there should be a sharp distinction between a student who is to become an analytical specialist and one who is not. The latter should, however, be taught to appreciate the background necessary for the specialist. A sharp distinction between inorganic and organic analysis is to be avoided. Some feel that quantitative analysis is taught too early, and that a better background in physical and organic chemistry and physics is required. If this belief is justified, quantitative courses could be more advantageously taught in the junior year. In any course it is considered important to acquaint the student with chemical and physical methods and the application of statistics to his results. It was felt that methods of sampling have been covered inadequately, if at all, and should be given a prominent place in the first course.

To accomplish these aims, the teacher must be able to present the subject with authority, enthusiasm, and a breadth of view. We all know of teachers who have done this in various branches of learning. We believe that many of those who teach analysis appreciate the philosophy and challenge of modern analysis, and will transfer this enthusiasm to the nonspecialist, so that he will appreciate the breadth and importance of the subject. Most important, this enthusiasm will draw those qualified by endowment and influence them to take up studies for advanced research in analytical chemistry.

L. T. HALLETT

RADIOACTIVE CONTAMINANTS IN TRACERS

Origin, Detection, Identification, and Removal

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The physical and chemical principles underlying the origin, detection, and removal of radioactive impurities in tracer materials are discussed from the standpoint of the individual user. Specific examples, drawn from every-day experience, are given as illustrations of all general causes, techniques, and procedures involved, to the end that tracer experiments may not suffer from the introduction of impurities and that the removal of impurities may be most conveniently and efficiently accomplished.

ONE of the most important technical advantages of radioisotopes, used either as tracers or as aids to analysis, is that identification and assay of a "labeled" atomic species may be made independently of the chemical form and the chemical nature of the matrix in which the species is located. This arises from the fact that the nuclear particles emitted by the decaying nuclei penetrate matter to varying degrees, permitting measurement at a distance from the source nuclei. Thus, phosphorus labeled with P^{32} may be identified and its content of P^{32} measured accurately, regardless of whether it is present as elemental phosphorus, sodium monohydrogen phosphate, an organic phosphate, etc., or whether the compound containing the P^{32} is contaminated with bone ash, carbonaceous material, water, etc. In so far as such simplifications in identification and assay can be made, the radioisotope technique is less tedious and time-consuming than such conventional analytical techniques as weighing or colorimetry; in the matter of tracing, where it shares the field with the stable isotopes, it is unique, provided, again, that the label can be accurately and positively identified.

The assumption implicit in simply putting samples under, or into, a counting device or ionization-measuring meter for radioisotope assay is that the activities measured come only from those nuclear species (nuclides) used to label certain elements or compounds at the start of the experiment, plus a natural background count or current which is constant for all samples (comparable to the tare in an experiment in which weighing is the method of measurement) and which may be subtracted, along with other corrections due to absorption, scattering, etc., to yield net activities proportional to the numbers of unstable atoms in the various samples. This basic assumption may no longer be valid when any radioactive species other than those knowingly added at the start of the experiment or normally occurring in the material being measured—e.g., naturally occurring K^{40}—is present without the knowledge of the experimenter.

In order to take fullest advantage of the technical simplicity of the radioisotope technique, radioactive impurities are preferably eliminated from the species to be used before the experiment is even started. Where this cannot be done—e.g., daughter radioisotopes, as in the case of 60-hour Y^{90} daughter of 25-year Sr^{90}—

elimination of any contribution by them to the final assays must be accomplished by the application of suitable physical or chemical procedures. The prerequisite to either approach is a knowledge of how radioactive impurities may arise, the steps normally taken to prevent their introduction (or to eliminate them if introduction cannot be prevented), the methods of detecting their presence, and some of the procedures that may be used to eliminate them, if present.

Because complete prescriptions for all contingencies cannot be given, even if space permitted, it is proposed to discuss the above items in principle, using actual situations, drawn principally from experience, as illustrations.

ORIGIN OF RADIOACTIVE CONTAMINANTS IN TRACERS

Qualitative Origin. Unwanted or undesirable (hence, by definition, contaminating) radionuclides may arise from any of the following contingencies: (1) the simultaneous activation, within the pile or cyclotron target, of nuclides other than that which gives rise to the desired radioisotope, such as nuclides of the same element, of associated elements, or of impurities; (2) nuclear reactions other than the one desired between the projectiles used and the target nuclide; (3) decay of the desired radionuclide (and of any others isotopic with it) to radionuclides with different chemical or physical properties, such as "daughter" activities continuously produced by the decay of the isotope or isotopes in question; and (4) contamination of the tracer, at any point in its preparation or use, with radioactive material originating from another source, such as contamination in the laboratory. Only the last-mentioned type of contamination is completely within the hands of the chemist to prevent; the others depend, to varying degrees, upon the nuclear properties of target and projectile species, which cannot be altered, or upon the physical vagaries of the creating instrument, which are not easily controlled.

Contamination Due to Other Nuclides in the Target. If it were possible to expose only that nuclide which could undergo the desired reaction with neutrons (or deutrons or alpha-particles), most contamination could be avoided. Unfortunately, most elements are polyisotopic—e.g., iron with four, tin with ten isotopes—all of which, in the absence of the requisite amounts of

separated isotopes (19), must be exposed whenever the bombardment of any one is desired. Thus, slow neutrons (to effect only the n,γ reaction) on any one give rise simultaneously, in the two cases mentioned, to 4-year Fe^{55} and 43-day Fe^{59} and to several tin activities. Inasmuch as the mixed radioisotopes of a single element may be used to trace that element (caution is required in the case of isomeric transition; see below), this is not a serious handicap. However, many elements are not conveniently exposed in the elemental form, because of such factors as chemical reactivity under the conditions of bombardment, such as phosphorus, difficulties in obtaining the elemental form, such as scandium, and difficulties in obtaining the element in sufficient purity with respect to elements of similar chemical properties—e.g., sodium metal free of potassium.

The use of a compound of the proposed target element may mitigate or eliminate these practical difficulties, but only at the cost of introducing all the nuclides of the other elements in the compound as possible sources of unwanted radioactivities. Hence, the most desirable compounds are the oxides (oxygen gives rise to minute quantities of 5000-year C^{14} under fast neutron bombardment but only to very short-lived activities with other standard projectiles), which are seldom immediately available in sufficiently pure form; nitrates and carbonates are favored second choices under those conditions (pile irradiation) where considerations of heat stability and mounting permit their use (again, only C^{14} is encountered as a contaminant). In cyclotron target fabrication, considerations of rigidity of mounting and of heat conduction may be paramount in determining the chemical form to be used. Anionic elements which are too volatile or otherwise awkward to be exposed as free elements or as their acids—e.g., chlorine—are most conveniently exposed as salts, in which case a cation is chosen which gives rise only to easily removed radiocontaminants—e.g., potassium. (A further consideration in the choice of chemical form, which is not pertinent to this discussion, is ease of postirradiation conversion to desired chemical forms.)

Chemical impurities, which are present to varying degrees in every target substance, are also subject to irradiation and activation. The quantitative contribution of each nuclide to the measured radioactivity of a target is not strictly proportional to the amount of it which is present, for each has its own cross section—i.e., probability of reaction—with respect to each type and energy of projectile. Thus even a 1% impurity of sodium in potassium will result, after pile (slow neutron) irradiation, in K^{42} contaminated to the extent of 13% with Na^{24}; after exposure of such potassium to deuterons in a cyclotron, the Na^{24} contamination may be nearly equal to the K^{42} desired. Pre-exposure contamination of calcium carbonate with 0.01% of calcium phosphate can result, after pile irradiation (39), in a 5% contamination of Ca^{45} with P^{32} (which, owing to the weak Ca^{45} β-radiation, may be magnified to an apparent 10 to 20%). Many other examples can be picked from an inspection of the literature (6, 39), but these are sufficient to illustrate the independence of chemical and radiochemical purity, and that the chief sources of radiochemical contaminants are those elements from which the exposed chemical is most difficult to separate.

Contamination Due to Other Nuclear Reactions. The various types of nuclear reactions which ensue when a single nuclide is exposed to neutrons, protons, deuterons, or helium ions are discussed elsewhere (7, 18, 28) and will not be described in detail here. In the pile, because of the low energy of most of its neutrons, n,γ is the predominant reaction, with a few well-known n,p and n,α reactions occurring at the lower end of the periodic table to give rise to radioactive species nonisotopic with, and hence contaminating, the n,γ product. Cyclotron radioisotope creation, because of the greater energies involved, gives rise to more radioactive species per nuclide exposed than does pile creation and, hence, to a greater degree of contamination with nonisotopic material. The faster neutrons available from cyclotrons give rise to a larger number of n,p and n,α reactions (creating $Z - 1$ and

$Z - 2$ nuclides, where Z is the atomic number of the parent), as well as $n,2n$ reactions to yield nuclides isotopic with the usually predominating n,γ product. Deuteron bombardments, even in the 40-inch and 60-inch cyclotrons, bring about d,n, $d,2n$, d,α reactions (giving $Z + 1$ and $Z - 1$ nuclides) as well as the more common d,p reaction (Z nuclide), while the higher energies obtained in the new outsize model at Berkeley (1, 27) give rise to radioisotopes of elements several columns removed in the periodic table, many of which have active daughters. Similarly, helium ions in the 20 to 40 m.e.v. range induce α,n, $\alpha,2n$, etc., reactions ($Z + 2$ product) and α,p, α,pn, and $\alpha,p2n$ reactions ($Z + 1$ product); in the 200 to 400 m.e.v. regions, a profusion of reactions takes place to yield nuclides of many elements of lower atomic number (1, 27).

Any of these reactions may take place with any nuclear species present in the target chemical to yield nuclides which may be radioactive. Thus, a cyclotron activation of iron with 20 m.e.v. deuterons will give: Fe^{55} and Fe^{59} from the d,p reaction, four cobalt isotopes from the d,n and $d,2n$ reactions, and three manganese isotopes from the d,α reaction; chromium, manganese, cobalt, and nickel activities from the same reactions upon impurities of these elements present in the iron itself; activities induced in the copper target plate, in traces of solder or other chemical contaminants used in mounting, etc. (18). Although the fission reaction gives rise to perhaps the most complex mixture of radioisotopes yet known, most pile—i.e., slow neutron—reactions are far less prolific; those (39) upon ruthenium to yield two ruthenium, one rhenium, and one technetium activity and upon potassium chloride to yield Cl^{36}, K^{42}, S^{35}, and P^{32} are among the worst in this regard. Pile irradiation has another advantage in that bonding to a metallic plate is not required (18); simple cans may be used to contain the target material, thus reducing the possibility of contamination with extraneous chemicals susceptible to activation.

Contamination Arising from Daughter Formation. Special attention is directed to those radioactive species which have radioactive daughters, whether these daughters are isotopic with the parent or not. The exposure of tellurium illustrates both cases. Tellurium has three nuclides which give rise to 90d Te^{127}, 32d Te^{129}, and 30h Te^{131} by n,γ or d,p reaction, the last-named decaying to the 8d I^{131}. Even the use of the two longer-lived radioisotopes of tellurium, after removal of the I^{131} by decay or other means, is hazardous (18), inasmuch as it is usually the beta-particles of the shorter-lived isomers of these (9.3h Te^{127} and 72m Te^{129}) which are measured; these originate from nuclei which may not be in the same chemical environment as were their parents, because of the translocation consequent upon the decay of the parent (22, 30, 33). Isomeric transition is thus to be regarded as a special case of contamination-by-daughter-formation in which the daughter is isotopic with the parent, in contrast to the usual case, of which the 25y Sr^{90}–60h Y^{90} and 65d Zr^{95}–35d Cb^{95} chains are examples.

Contamination with Extraneous Sources. Radioactive contaminants arising from undesired nuclear reactions in the target element itself cannot be prevented by the production radiochemist, whereas those arising from associated ions or impurities are largely controllable by him through pre-exposure choice of chemical form and purity. He has no control whatsoever over contamination by daughter formation or contamination arising by accidental introduction of other radioactive material into the product after it has left his hands. Both kinds of contamination, the one arising as an inexorable consequence of decay, the other by human error, must be reckoned with by the user and either prevented where possible or cured where not.

Contamination by daughter formation can be anticipated by the user from a knowledge of the decay scheme (7, 18, 24, 28, 39) of each radioisotope being used. Contamination by the introduction, before or during use, of other radioactive species can and should be prevented by the user in the same manner as he prevents the contamination of his c.p. reagents, with additional pre-

cautionary measures necessitated by the range of specific activities, half-lives, and radiation energies encountered among the species which may exist in his laboratory. The principles of prevention of this type of contamination are similar to those for the prevention of the contamination of personnel and equipment discussed elsewhere (*21, 32, 36*), summarized succinctly by the term "aseptic technique," and will not be dwelt upon here. The principles of detection and elimination, once contamination has occurred, are discussed below.

DETECTION AND IDENTIFICATION OF RADIOACTIVE IMPURITIES IN TRACERS

Because there exist many unpreventable and (to a degree) unforeseeable types of contamination, methods of detection and of identification should be at hand in every laboratory using tracer material. These may be divided into two categories: (1) methods involving the physical characteristics of the several radioactive species (decay schemes, half-lives, radiation type, radiation energies); and (2) methods involving the chemical characteristics of the several radioactive elements present. As it is usually only in so far as they interfere with physical measurement that they are undesirable, it may be anticipated that the physical detection of radioactive impurities is the more important. However, according to the degree to which the system being studied may concentrate the impurities (this depending upon chemical properties), identification of the chemical nature of the impurity must be made. Chemical identification will also be necessary if chemical removal of the impurity is required. Thus, if K^{42} is used as a tracer for entrained water droplets in an air stream (one actual application in progress), the measurements are independent of Na^{24} impurity. However, when used in mammalian organisms to determine the rate at which potassium leaves the plasma and extracellular fluid, Na^{24} to the extent of even 1% (which is within the limits of error of radioactive assay) cannot be tolerated, for it will remain almost entirely in this phase while K^{42} will disappear from it almost completely (*10, 11, 14, 17*). Chemical identification is thus necessary to establish the degree of importance of the impurity in the chemical studies to be made and, as in the case quoted, to an effective removal of the impurity.

The detection of radioactive impurities is facilitated by a knowledge of what radioactive species may be present; this has been discussed in the preceding section. Thus, sodium, rubidium, and cesium activities may be anticipated in irradiated potassium because of the difficulties attendant upon procuring sufficiently pure potassium or potassium salts for exposure; a laboratory using P^{32} and K^{42} may well anticipate a degree of contamination of the latter with the former; deuteron-irradiated iron may contain certain radioactive impurities not present in pile-irradiated ion; and so forth. Following such a preliminary survey of the active species anticipated, their physical and chemical properties may be listed and suitable detection measures devised.

Physical Methods of Detection and Identification. Perhaps the most foolproof physical method of detection is based on considerations of half-lives. A sample of Na^{24} exhibiting a half-life of longer or shorter than 14.8 hours, at any time after the end of activation and under any condition of measurement, contains a radioactive impurity of half-life longer or shorter, respectively, than 14.8 hours. Theoretically, such a half-life determination cannot fail to detect an impurity except (1) where the impurity has the same half-life (within the error of measurement), or (2) where a daughter element, the growth and decay of which in the system may have no relation to its true half-life, is being formed from its parent. An example of the first of these exceptions is again Na^{24} in K^{42}; the similar half-lives of 14.8 and 12.4 hours (not known or easily measurable with the degree of accuracy indicated by the quoted figures) do not lend themselves to easy detection of the impurity, much less to its quantitative assay. [The need for more accurate measurements, over long periods, of both

half-lives and absorption characteristics of even the most common radioisotopes is admirably illustrated by the recent discovery (*13, 25*) of the $58d$ I^{125} in the mixture of iodine and tellurium isotopes formed by the action of deuterons on tellurium to produce $8d$ I^{131}. The presence of this isotope in tellurium targets (and in the active iodine isolated therefrom) had been overlooked during the many years that $8d$ I^{131} had been in use.] A different story is $14.3d$ P^{32} impurity in K^{42}, for half of it will still be present when less than 10^{-6} part of the original K^{42} is left; a corollary of this calculation is that extremely minute impurities ($<10^{-6}$) of P^{32} in K^{42} can be assayed by a simple decay procedure. This method, as well as others described in this section, is an example of what is termed "activation analysis" (*5, 29*), which may be defined as the estimation of a chemical impurity by measurement of the radiations emitted by it after exposure in a pile or cyclotron.

However, turning to the second exception listed above, the detection of $40h$ La^{140} in the presence of its $12.5d$ Ba^{140} parent cannot be guaranteed by this method alone, even though it is known (from experiments using the other methods discussed below) to be present, for it is a consequence of the exponential nature of radioactive decay (*16, 26*) that a shorter-lived daughter will first "grow" from its longer-lived parent (thus giving an increase in the total radioactivity of the parent-daughter system) until radioactive equilibrium is reached, following which it will decay with the half-life of its parent. Such observations, when added to other data on a given system, can be used to identify and estimate an impurity but they cannot be relied upon by themselves. A longer-lived daughter will, after the decay of its shorter-lived parent to undetectable levels, be a single species capable of detection by this means; until that time, the system will exhibit a continuously changing half-life, in itself evidence of more than one radioactive component.

The second type of physical detection of impurities rests upon the elucidation of the types and energies of radiations (*16, 26*) (commonly termed the "absorption" characteristics) of the mixture. The presence of γ- or x-radiation in a tracer known to be a pure β-emitter is evidence of an impurity which may or may not itself be a β-emitter of the same or differing half-life. Such electromagnetic radiations, inefficiently measured by most β-measuring devices, arise as a consequence of decay ($\beta\gamma$; isomeric transition; electron capture) (*7, 18, 28*) but may arise independently from extranuclear reactions under the conditions of measurement ("bremsstrahlung"); when the latter is the case, the demonstration of x- or γ-radiation in a sample is an artifact and affords nothing in the way of proving the presence of an impurity. Similarly, it is more difficult to distinguish between a "hard" β- and a weak γ- or x-ray and between weak β-rays and conversion electrons than between β-rays and γ-rays or between β-rays or γ-rays of sufficiently different energies.

The demonstration of β-ray (or γ-ray) spectra of differing energies is most commonly done by measuring the relative diminution of the activity of a sample by the interposition, between sample and counter, of aluminum (or lead, for γ-rays) sheets of varying, known thicknesses. A plot of observed activity against thickness of absorber (the so-called absorption curve) permits a specification of the maximum energy of the β-spectrum (or energy of the homogeneous γ-rays). In those cases where the maximum energies of the β-spectra are sufficiently different and the spectrum of each component is not too complex, absorption measurements can serve as a means of identifying β-active impurities. Multiple spectra, as in the case of Zr^{95} which has two β-spectra with maximum energies of 0.394 and 1.0 m.e.v. and abundances of 98 and 2%, respectively, and γ-radiation (in addition to its Cb^{95} daughter), or of La^{140} with three β- and five γ-spectra of various energies and amounts, make such methods of detection, based on graphical analysis, much more difficult. Although γ-rays are of uniform energy and therefore yield strictly exponential absorption curves, multiple spectra are all too common to permit free use of this method. As decay schemes and β-ray spectra become more

accurately defined and as "standard" absorption curves are accumulated within tracer-using laboratories, the absorption-curve method of detecting, identifying, and quantitating a radioactive impurity will become more useful. (It is assumed that β-ray spectrometers and coincidence counters, more accurate instruments in this regard, will not become common in tracer-using laboratories.) At present, it can be used only in those cases where there is sufficient information on these points and where those measuring conditions which influence the assay of radioactivity (type of instrument, amount of scatter, location of absorber with respect to counter window, etc.) are either held constant or otherwise controlled. The shape of an absorption curve is markedly dependent on these measuring conditions which vary greatly from laboratory to laboratory, even within the same institution.

Chemical Methods of Detection and Identification. As tracers are generally used in experiments which are based upon their chemical properties, it is possible, although in general more laborious, to employ chemical methods for the detection, as well as for the identification and removal, of radioactive impurities. Such methods depend upon the segregation, through chemical manipulation, of the major constituent or of each minor constituent. Such segregation being a necessary eventuality in the removal of impurities, methods for achieving this are discussed in the section on Removal.

REMOVAL OF RADIOACTIVE IMPURITIES IN TRACERS

Radioactive impurities are usually of significance only because of their contribution to the measured activity of samples taken from the system under observation (an exception would be a case in which the radiation from such an impurity exerted a significant photochemical or biological effect upon the system under observation). In so far as this is true, radioactive impurities may be eliminated from the experiment or quantitated, so that their contribution to radioactive assay can be subtracted, by methods other than chemical segregation. The physical properties of half-life, type of radiation, and energy of radiation, which are discussed above, may lend themselves to the practical elimination of an impurity by relatively simple decay or radiation-absorption procedures. Where applicable, such physical procedures (which remove the offending impurity from consideration, if not always from the experiment) are more desirable than chemical separation procedures.

Physical Methods for the Removal or Quantitation of an Impurity. DIFFERENTIAL DECAY, which allows the radioactive impurity to remove itself from the system, is most simply applied where the impurity has a half-life much less than that of the desired radioisotope. Thus, in the production of P^{32} by the n,γ reaction on P^{31}, potassium dihydrogen phosphate can be used as the target substance, for the 12.4-hour K^{42} simultaneously produced in it will decay into insignificance in a few days while the 14.3-day P^{32} will decay only to the extent of 5% per day (see calculation under Detection). Similarly, the P^{32} produced in 180-day Ca^{45} by the n,γ reaction on calcium carbonate which contains phosphate as an impurity can be eliminated by simply waiting.

As far as accuracy of physical measurement of radioactivity is concerned, the waiting period can come before, during, or after the use of the material as a tracer in an experiment, as long as it occurs before the final measurement of any sample. The only exception to the latter statement is in the case of radioactive daughter formation, whether the daughter is isomeric with the parent or not, where the daughter has half-life of significance relative to the time phenomena being studied. Isomeric daughters (such as the shorter-lived Te^{127} and Te^{129} isotopes discussed under Origin), occurring as a result of decay by isomeric transition, may not remain or be found in the same chemical loci as their parents (*18, 22, 30, 33*). Thus, the radioactivity of the daughter may not come from the chemical forms which resulted from the chemical transformations undergone by the parent prior

to its decay—and it is usually these transformations which it is desired to observe.

The case of nonisotopic daughter formation is more obvious. The weak β-emitting 25-year Sr^{90} is usually measured by the energetic β-radiation of its 60-hour Y^{90} daughter. If Sr^{90} is used to trace strontium in a system which can translocate Y^{90}, the radiation of the latter may be found at quite different points or in quite different compounds than the radiation of the parent Sr^{90}, thus giving rise to an erroneous assignment of Sr^{90} location. In this case, as in that of the tellurium isotopes mentioned above, the simplest remedy is still removal by decay, but the period of waiting must take place between the time of final sample preparation and that of radiation measurement. During this period, translocation of daughter from the sample is prevented by the very act of sampling, while decay of isolated daughter and growth of new daughter from the sampled parent take place until the state of "radioactive equilibrium" is again attained, permitting use of the daughter radiation to quantitate the parent. The waiting period necessary depends upon the relative half-lives; in the cases of Te^{127} and Sr^{90}, a few hours and a few weeks, respectively, suffice to achieve 95% of the equilibrium (final) value.

A shorter waiting period may be used if one is willing to make two or more measurements on each sample and calculate the equilibrium or independent values of each component from the standard equations (*16, 26*) defining the relation of parent and daughter activities as a function of time or, in the case of two or more independent components, by use of the equation defining the total activity (Q) at any time of measurement (t) as the sum of the individual contributions ($Q_1e^{-\lambda_1 t}$, $Q_2e^{-\lambda_2 t}$, etc.). It is evident that the practice of allowing impurities to decay to a negligible activity is simply a special case of this equation, in which the corresponding $e^{-\lambda t}$ values become $e^{-\infty}$, or zero, relative to the major constituent.

DIFFERENTIAL ABSORPTION. The elimination of a radioactive impurity by means of its radiation absorption characteristics is as simple as elimination by decay; it has the additional practical advantage of occasioning less loss of time, as no waiting period is involved. This method can be applied either when the characteristic energies (or types) of radiation differ sufficiently to allow an independent assay of the major constituent under conditions which permit no contribution of the minor ones, thus requiring only one measurement per sample, or when a calculation of the activity of the major constituent can be made from two or more measurements on each sample under differing conditions of relative absorption; each such measurement is thus the sum of the relative contributions of more than one component.

The simplest of these two situations exists when the radiation of the major constituent is sufficiently more energetic than that of the impurities to allow it to be measured through a thickness of absorber which absorbs all of the radiation from the impurities. Many such cases are known. The common use of uranium for counter and electroscope calibration takes advantage of UX2, in equilibrium with either its parent, UX1, or grandparent, 4.56 × 10^9-year U^{238}; the weak radiations of both antecedents can be completely absorbed by the interposition of about 50 mg. per sq. cm. of aluminum, which absorbs only about 25% of the UX2 β-radiation. We are thus able, in effect, to synthesize a source with strong β-radiation and infinite half-life, a situation that does not exist in nature.

One case in which elimination by absorption is practically essential to usage is that of the 28-day Ce^{141} and 33-hour Ce^{143}, created by the n,γ reaction on cerium. Both of these emit β- and γ-radiation and the latter gives rise to the β-emitting 13.8-day Pr^{143}. The mixture can still be used for cerium tracing if all measurements are made through a thickness of absorber sufficient to stop all β-radiation from the Pr^{143}, thus measuring only the γ-rays from the two cerium isotopes. Similarly, P^{32} produced by the n,p reaction on sulfur can be measured independently of the simultaneously produced, longer lived S^{35} by the use of absorbers, even though both are pure β-emitters.

When the types and energies of radiation emitted by major constituent and an impurity are such that the contribution of the latter cannot be completely eliminated, it may still be possible to analyze each sample radiometrically by absorption techniques. The case of 65-day Zr^{95} and its 35-day Cb^{95} daughter, both of which emit β-rays and γ-rays, may serve as an example.

To analyze such a mixture for Zr^{95} we require two measurements on each sample. The first of these is a simple gamma-ray measurement, taken through sufficient absorber (> 400 mg. per sq. cm. of aluminum) to stop all β-radiation from the sample. The second measurement must be taken through sufficient absorber (ca. 30 mg. per sq. cm. of aluminum) to screen out the weaker Cb^{95} β-rays but let as much of the Zr^{95} β-rays through as possible. The observed radiation in the second measurement is then the sum of part of the Zr^{95} β-spectrum and essentially all of the Zr^{95} and Cb^{95} γ-spectra; the latter, evaluated by the first measurement, can be subtracted to yield that fraction of the total Zr^{95} β-radiation which penetrates the absorber used in the second measurement. If a relative zirconium count is all that is required, we may stop at this point, although, by reference to a standard β-absorption curve of pure Zr^{95} (obtained in the same laboratory under the same conditions, since β-absorption curves are not exponentials of the $e^{-\lambda t}$ type characteristic of decay curves and are markedly influenced by the particular assay setup used), the count of Zr^{95} under other conditions of absorption may be derived. If the amount of Cb^{95} present is also desired, a third measurement on the sample, taken with minimum absorber present, can be made. [An alternative method, making use of the $\beta:\gamma$ ratio of purified Zr^{95} instead of a third measurement on each sample, is possible (4). In such a method, columbium is measured by its γ-radiation rather than by its weak β.] The assay at this point is corrected first for γ-radiation and then, by reference to an independently derived Zr^{95} β-absorption curve, for the contribution of Zr^{95} β-rays under the conditions of the third measurement, to yield the Cb^{95} β-count under the latter conditions.

It is evident that, when the proper conditions exist, the analysis (effectively a separation) of an n-component mixture by either decay or absorption requires $n + 1$ measurements on each sample plus n reliable decay or absorption curves; in those special cases where individual components can be allowed to decay to a negligible activity or can be absorbed completely, leaving a measurable activity of the others, the $n + 1$ measurements are reduced by one for each component thus eliminated.

Chemical Methods for Removal or Estimation of an Impurity. It is possible to have mixtures in which the nuclear characteristics of the radioisotopes present do not lend themselves to independent assay with sufficient accuracy or ease by either differential decay or absorption, or where the effects induced by the radiation of minor constituents cannot be overlooked. In such cases, chemical removal of the offending nuclides must be effected at some time prior to the final measurement of the samples. If the contaminants are not isotopic with the major constituents and are not daughters of them, removal may be effected at any time prior to measurement. If they are nonisotopic daughters, removal after sampling but before measurement is necessary. If they are isotopic daughters (isomers), chemical removal cannot be made; such cases must be handled by the physical methods discussed above.

Methods for the chemical removal of radioactive contaminants depend, of course, upon the chemical characteristics of the species involved. However, they may be divided into two general categories: (1) that in which the chemical forms of both major constituent and impurity, or impurities, are present in macroscopic amount; and (2) that in which one or more of the chemical forms of any of the radioactive constituents of interest is present in submacroscopic amount. (A macroscopic amount may be semiquantitatively defined as that amount which will give a visible or filterable precipitate under usual conditions of laboratory procedure and which does not require, except for convenience, the special techniques of "trace chemistry" or radiochemistry in the course of isolation and/or removal from the mixture.) It is not feasible to discuss methods for the purification of tracers which

fall into the first category, or which can conveniently (through the addition of "carrier") be put into it, for these are as varied and common as the fields of analytical and purification chemistry. Furthermore, radiochemistry has little, except the convenience of the tracer technique itself, to offer in this class of separations.

The second category of chemical separation, where a chemical species of considerable radioactive contribution but relatively negligible mass must be segregated, has received much attention from radiochemists in general and, particularly in recent years, from those concerned with the preparation of pure, "carrier-free" tracers. (The practical impossibility of proving the absence of isotopic carrier in every radioisotope preparation has led to an interpretation of the term "carrier-free" somewhat as follows: Every practical step is taken to avoid the introduction of isotopic carrier in target or reagent materials used to prepare the product.)

This type of problem is distinguished by the necessity of removing submacroscopic (microgram) constituents from macroscopic constituents (gram), the mass of which exceeds the former by factors of 10^6 to 10^8, and/or separating submacroscopic constituents from each other. Perhaps the most complex examples are afforded by the separation of individual fission products (39) from neutron-irradiated uranium, which requires the isolation, in high yield, of each of over a dozen submacroscopic species from each other as well as from the coexisting macroscopic species (parent uranium and co-formed plutonium), and by the separation of each component of a mixture of rare-earth radioisotopes (15, 20, 35), some present with and some without carrier. In less dramatic but still illustrative form, it is exemplified by the isolation, without the addition of phosphate carrier, of a curie of P^{32} (3.5 micrograms) from 2 kg. of pile-exposed sulfur (8) or of 100 mc. of I^{131} from 50 grams of tellurium (3).

In production processes of this type, emphasis is placed upon the recovery of a submacroscopic constituent rather than upon its removal as an impurity. It is only in those cases where removal is most easily effected by a process designed principally for recovery that a recovery process, developed to operate without recourse to carriers, is desirable as a removal or purification process. Hence, the possible application of radioisotope production experience to the problem of purification of tracers will revolve about procedures designed to recover minor components rather than to discard them.

The principal types of methods in general use for the isolation and radiochemical purification of carrier-free tracers are: (1) coprecipitation with nonisotopic carrier; (2) ion-exchange adsorption and elution; (3) solvent extraction; and (4) volatilization or distillation. Electrolytic methods have not been developed to the same extent as these four, although there is no *a priori* reason why they should not be.

COPRECIPITATION depends upon the possibility of forming a precipitate in a solution of the desired radioelement which will carry the latter out of solution, even though none of the reagents added contain stable isotopes of it. This last condition implies that the carrying precipitate and the radioisotope must be separable in a subsequent step to yield the radioisotope in a desirable form.

One type of coprecipitation is exemplified by the use of ferric hydroxide or lanthanum hydroxide, formed by adding first ferric or lanthanum ion and then ammonium hydroxide, to carry P^{32} as phosphate out of a solution containing impurities that are soluble under these conditions (8); after solution of the hydroxide precipitate in hydrochloric acid, the cation is exchanged for hydrogen ion by isopropyl ether extraction (in the case of iron) or a cation-exchanger, thus giving a solution of P^{32} in hydrochloric acid, or the iron or lanthanum may be removed by precipitation with strong sodium hydroxide, leaving a solution of P^{32} in sodium hydroxide. A different type of coprecipitation is the use of lead to carry barium and strontium out of solution as lead sulfate or as lead nitrate, the lead subsequently being separated as lead sulfide or lead chloride, or by ion exchange (38).

This type of carrying depends upon isomorphism in crystal structure, whereas that of $P^{32}O_4^{---}$ by trivalent hydroxides is

termed "scavenging" because of its relative nonspecificity. Practically every trivalent ion (and many divalent ones, particularly if carbonate is present) in a solution from which ferric hydroxide is precipitated by ammonium hydroxide will go down with the precipitate; this can be a useful decontamination step if the desired constituent is an alkali metal or, for other reason, soluble under the conditions of the precipitation. Such is not the case when specific crystals are formed, as in lead nitrate precipitation, and these methods are best used to segregate specific major constituents, leaving the minor ones in solution.

ION-EXCHANGE columns as separators have been developed to a high degree within the Plutonium Project (15, 20, 35). Although initially applied (9, 34) to the isolation of each component of a mixture of traces of elements (the fission products), the method of "complex elution" from an ion exchanger has been shown to be not only sensitive enough to separate neighboring rare earths (15) but of practical use in the separation of macroscopic amounts of these materials from each other (31). It can also be used to separate macroscopic from submacroscopic amounts (20), an application that is immediately useful in the usual purification problem.

Two examples of current usage of ion-exchange columns to remove macroscopic impurities from tracers may be given as illustrations. In one (mentioned above), a solution of many milligrams of lanthanum ion in dilute hydrochloric acid containing carrier-free P^{32} as phosphate is passed through a (previously acidified) cation-exchange column, large enough to substitute hydrogen ion for all the lanthanum ion present; the effluent contains all the P^{32} in hydrochloric acid solution. (The column will also pick up other cationic species present in the starting solution.) Similarly, carrier-free S^{35} (as sulfate) is freed of its parent potassium chloride by exchange of potassium for hydrogen ion in such a column, following which hydrochloric acid is evaporated to leave $H_2S^{35}O_4$. The general principle behind these applications is the ion-exchange conversion of nonvolatile constituents into volatile ones which are then evaporated.

SOLVENT EXTRACTION. The same principle underlies the use of ether extraction to remove ferric ion, previously added as carrier and, hence, an impurity. The conversion of ferric chloride to hydrochloric acid by ether extraction is entirely analogous to that of lanthanum chloride and potassium chloride to hydrochloric acid, described above, by ion exchange. The use of specific complex-forming agents (such as acetylacetone) in solvent extraction to differentiate between two or more coexisting species is likewise analogous to the use of complexing anions—e.g., citrate—used to separate species from ion exchangers. In such differentiation, the removed component is replaced by hydrogen ion. If it is desired to recover it, it is readsorbed (9) (or re-extracted) and recovered in a solution contaning no nonvolatile impurity.

VOLATILIZATION has been mentioned as a means of removing a volatile macroscopic impurity (hydrochloric acid, in the cases outlined). It may also be used to remove a submacroscopic constituent. Procedures of this type are utilized to recover C^{14} and I^{131} without added carrier from their bulk parents, but precisely the same methods could be applied to remove those same radioisotopes if they were considered to be impurities.

C^{14} exists as (or is easily converted to) carbon dioxide or other volatile forms in the nitrogenous materials commonly used as targets for the reaction N^{14} (n,p) C^{14}. Upon acidification of the mixture of bulk parent and reagents and the trace of C^{14}, the $C^{14}O_2$ may be swept out of solution by a stream of nonisotopic gas (water, nitrogen, etc.) and collected as such or in a more desirable form (2, 12, 23, 37). I^{131}, created by the decay of its Te^{131} parent after the exposure of tellurium to neutrons or deuterons, can be volatilized and recovered in pure form from a solution of the parent following conversion of the constituents to suitable chemical states (tellurate and iodine) (3). Volatilization can also be used to remove carrier-free ruthenium from mixtures by conversion to the volatile form, RuO_4.

From the examples, it can be seen that methods for the separation of contaminating radioactive impurities from tracers are potentially as many and varied as are the usual chemical separation methods appearing in the literature. The method and extent of purification in any given instance, whether chemical or radioactive purity is the objective, will depend upon the nature of the specific mixture at hand and also upon the use to which it will be put, for the latter will set the quantitative interpretation of the word "pure." However, each user should have at hand the knowledge, techniques, and instruments necessary to establish and observe his own criteria of purity.

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DETERMINATION OF SILICA

In the Presence of Fluorine and Phosphorus

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Two methods have been developed for the determination of silica in the presence of fluorine. In a photometric procedure for the analysis of high-purity hydrofluoric acid, the molybdenum-blue reaction is utilized in the determination of from 0.0 to 1.0 mg. of silica in the presence of as much as 0.8 gram of fluorine. The fluorine is complexed with boric acid. One hour is required for an analysis, and results are reproducible within 0.02 mg. of silica. A gravimetric procedure, in which silica is weighed as the oxine salt of molybdisilicic acid, is adapted to the analysis of fluorine compounds such as sodium fluosilicate, cryolite, and fluorspar. Through use of a correction factor, the method also may be used in the analysis of samples contaminated with phosphates, which precipitate quantitatively as the oxine salt of molybdiphosphoric acid. Detailed information is given on the decomposition of samples for analysis, interfering elements, the determination of gravimetric factors, and the precision and accuracy of the method in the analysis of various fluorine-containing materials.

IN RESEARCH on methods for the recovery of by-product fluorine from the processing of phosphate rock, analytical methods were needed for the determination of various quantities of silica in the presence of proportionately large amounts of fluorine. It was deemed essential that the method also be applicable in the presence of phosphates.

The only method that has gained wide usage for the determination of silica in the presence of fluorine is the classical method of Berzelius or a modification of it (*12*). Some investigators (*12, 23*) have tried using boric acid to convert fluorine to the fluoborate form prior to dehydration of the silica, but this technique yields low results if the sample requires fusion for solution, and the silica cannot be freed entirely of contaminative boron (*12*).

A volumetric method has been used for the determination of fluosilicic acid in anhydrous hydrofluoric acid (*25*). Vasil'ev and Barinova (*27*) determined traces of silica colorimetrically as molybdisilicic acid in fluorine-containing solutions of sodium aluminate. The results were good, provided aluminum was present in twice the amount necessary to form cryolite with the fluorine. Boric acid also has been used to complex fluorine prior to the determination of silica by the molybdisilicic acid method (*9*) and phosphorus by the molybdenum blue method (*16*).

Volumetric (*10, 20, 27, 30*) and gravimetric (*28*) methods based on the formation of a precipitate composed of molybdisilicic acid and 8-hydroxyquinoline (oxine) are described for the analysis of silicates. Vasil'ev and Barinova (*27*) state that the volumetric method is applicable in the presence of fluorides, provided sufficient aluminum is present. The analogous reaction of phosphorus has been used for the volumetric (*3, 6, 7, 8, 19, 21, 31*) and gravimetric (*22, 24*) determination of this element. King and Watson (*14*) described a gravimetric method in which the silica is precipitated as the pyramidone salt of molybdisilicic acid.

None of the methods described in the literature as being based upon precipitation of silica as the oxine salt of molybdisilicic acid would be applicable in the presence of phosphates. A method for the determination of silica in phosphorus-free materials would have some value but could not be used for the analysis of products from a fluorine-recovery system in a phosphate plant.

The present paper describes the development of a gravimetric method in which the oxine salt of molybdisilicic acid is utilized for the determination of silica in the presence of fluorine and phosphorus. A photometric method, based on the molybdenum-blue reaction, is also described.

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APPARATUS

A filter photometer (Fisher A.-C. electrophotometer) fitted with a 650-mμ red filter and 2-cm. absorption cells.

A glass-electrode apparatus (Leeds & Northrup Universal pH potentiometer).

Selas filtering crucibles, medium porosity, 30-ml. capacity.

Wooden or, preferably, Teflon plastic stirring rods with rubber tips.

Bakelite burets.

Hard rubber bottles.

REAGENTS

In both procedures, the following reagents are required: Hydrochloric acid, 1 + 9. Acetic acid, 1 + 2. Boric acid.

Ammonium Molybdate Solution. Dissolve 50 grams of the salt, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 500 ml. of water, allow to stand 24 hours, and filter. Use within a week.

Thymol Blue Indicator Solution. Dissolve 0.4 gram of thymol blue in 10 ml. of freshly prepared 5% sodium hydroxide solution in a 300-ml. platinum dish. Dilute to 250 ml. and neutralize with dilute hydrochloric acid to an orange color; avoid excess acid lest the indicator be precipitated. Dilute the solution to 500 ml. in a volumetric flask.

Sodium Sulfite Solution. Dissolve 170 grams of the anhydrous salt in about 900 ml. of water. Filter and dilute to 1000 ml.

For the gravimetric procedure provide the following additional reagents:

Hydrochloric acid, 1 + 1 and 1 + 20.

8-Hydroxyquinoline Solution. Dissolve 14 grams of oxine in 20 ml. of 6 N hydrochloric acid, dilute to 100 ml., filter, and dilute the filtrate to 1 liter.

Saturated Wash Solution. Dilute a mixture of 12 ml. of glacial acetic acid and 143 ml. of concentrated hydrochloric acid to 2 liters. Fuse a 0.25-gram sample of quartz with sodium hydroxide. Proceed as described below for phosphate rock, with the exception that the boric acid need not be added. Precipitate the silica from six 50-ml. aliquots (about 25 mg. of silica in each) and filter. Transfer a portion of the unwashed precipitate to a 1-liter round-bottomed flask, and add about 800 ml. of the acid solution. Boil for 10 minutes under a reflux condenser. If all the precipitate dissolves, cool slightly, add additional precipitate, and continue heating. Cool to room temperature, allow to stand overnight, and filter just before use.

NOTE. The expressions (1 + 9), etc., refer to dilutions by volume with distilled water. Thus hydrochloric acid (1 + 9) would be prepared by adding one volume of concentrated hydrochloric acid to nine volumes of water.

PHOTOMETRIC PROCEDURE

The photometric method is intended solely for the determination of silica in high-purity hydrofluoric acid. Phosphates inter-

fere, and compounds that are insoluble in a weakly acidic solution must be absent.

The method is suitable for the determination of from 0.0 to 1.0 mg. of silica in the presence of not more than 0.8 gram of fluorine. Larger proportions of fluorine lessen the color intensity because of incomplete conversion of the silica to molybdisilicic acid.

Determination of Silica in Hydrofluoric Acid. Dissolve about 2.8 grams (20 pellets) of sodium hydroxide in 100 ml. of water in a 300-ml. platinum dish. From a Bakelite buret, add an aliquot of hydrofluoric acid containing not more than 0.8 gram of fluorine to the alkaline solution. The acid should be sufficiently dilute to make errors in measurement insignificant. If prior quantitative dilution of the acid is necessary, the volumes can be assumed to be additive.

Dilute the solution in the dish to 170 ml., add 8 grams of boric acid, and stir to clarity with a rubber-tipped Teflon stirring rod. Add 8 drops of thymol blue indicator and concentrated hydrochloric acid, dropwise, until the solution becomes yellow. Do not bring the color of the indicator to red. Add hydrochloric acid (1 + 9) from a buret, stirring constantly until the indicator assumes a permanent pink color. Add 5.0 ml. of hydrochloric acid (1 + 9), 5.0 ml. of acetic acid (1 + 2), and 5.0 ml. of 10% ammonium molybdate solution in the succession named. Stir the solution between additions of reagents, and stir vigorously after the addition of the molybdate.

Wait 5 minutes for the formation of the molybdisilicic acid, then reduce it to molybdenum blue by adding slowly from a pipet, with vigorous stirring, 20 ml. of 17% sodium sulfite solution. Dilute to 250 ml. in a volumetric flask, and mix thoroughly. Thirty minutes after the addition of sulfite, determine the color intensity of the solution with the photometer. Use distilled water in the reference cell. Read the amount of silica from the calibration curve described below.

Preparation of Calibration Curve. Fuse 0.1008 gram of Bureau of Standards glass sand 81 with sodium hydroxide and disintegrate the melt in the manner described for phosphate rock. Dilute the acidified solution to 1 liter (1 ml. ≈ 0.1 mg. of silica). Use aliquots of this solution to determine 10 points, with a blank as the eleventh point, on the calibration curve in steps of 0.1 mg. of silica. Put the aliquots through the procedure given for the analysis of hydrofluoric acid.

Construct a calibration curve, plotting silica concentration against color intensity. Inasmuch as this curve includes the silica derived from the sodium hydroxide and other reagents, draw a corrected curve, beginning at 100% transmittancy and paralleling the original curve. Determine and subtract a blank from the corrected calibration curve for each new set of reagents.

GRAVIMETRIC PROCEDURE

The working range of the gravimetric method is from 0.5 to 40 mg. of silica, but the range from 5 to 25 mg. is recommended. Precipitates containing more than 25 mg. of silica weigh more than 1 gram and are more difficult to filter, wash, and dry than those in the optimum range.

The method is suited to the analysis of complex fluorides in which silica is a major constituent. Phosphates, if present, are precipitated along with the silica and necessitate a correction in the weight of the precipitate to obtain the percentage of silica. Germanium, vanadium, and pentavalent arsenic form analogous compounds and must be absent.

Preparation of Samples. Solutions containing fluorine should be handled in platinum whenever possible. Alkaline solutions, in particular, attack glassware and should be handled entirely in platinum. Slightly acid fluoride solutions that contain a relatively large proportion of boric acid may be handled for a short time in glassware without a significant accretion in silica content. Silica may precipitate during the neutralization of alkaline solutions. The difficulty can be avoided by diluting the solution and by keeping it cool during the addition of acid. On standing, silicic acid polymerizes (26) and reacts incompletely with ammonium molybdate. To avoid this difficulty, samples are made strongly alkaline just prior to the pH adjustment which precedes the formation of the molybdisilicic acid complex.

HYDROFLUOSILICIC ACID OR HYDROFLUORIC ACID CONTAMINATED WITH SILICA. Dissolve about 2.8 grams (20 pellets) of sodium hydroxide in 100 ml. of water in a 500-ml. platinum dish. Add a sample of the acid that contains between 5 and 25 mg. of silica and not more than 0.8 gram of fluorine. Dilution and transfer of the sample are made best on a gravimetric basis. Hard rubber bottles are satisfactory containers for the acids. Add 8 grams of boric acid, dilute to 170 ml., and stir until it dissolves.

SODIUM FLUOSILICATE. To a 0.1000-gram sample in a 300-ml. platinum dish, add about 2.8 grams (20 pellets) of sodium hydroxide, and dissolve the mixture in 100 ml. of water. Add 4 grams of boric acid, dilute to 170 ml., and stir until it dissolves.

CRYOLITE OR FLUORSPAR. Fuse 4 grams (30 pellets) of sodium hydroxide in a silver crucible, cool to room temperature, and place the analytical charge of 0.5000 gram on top of the melt. Add another 4 grams of sodium hydroxide and 2 ml. of ethyl alcohol.

Heat the crucible on a hot plate at a temperature that will evaporate the alcohol gently, then heat at the full temperature of the hot plate for a few minutes. Heat the charge to slight effervescence over a Bunsen burner. As effervescence ceases, increase the heat until the bottom of the crucible is a dull red, and continue heating at this temperature for 5 minutes. A coating of silver oxide often makes it difficult to determine when the bottom of the crucible is red. Reasonably close control of temperature is necessary to ensure complete decomposition of the sample without excessive attack upon the crucible. At the proper temperature the melt is reddish brown.

Cool the crucible to room temperature, transfer to a 300-ml. platinum dish, and add 100 ml. of warm water (60° C.). Remove the crucible, wash it with a jet of hot water, then with hydrochloric acid (1 + 20), and police thoroughly. Add 2 ml. of 30% hydrogen peroxide, and digest the solution somewhat below its boiling point for 10 minutes, then cool to 25° C., and dissolve 8 grams of boric acid therein. Add 8 drops of thymol blue indicator solution, then concentrated hydrochloric acid, dropwise, until the color changes from yellow to red. Add 8 ml. of hydrochloric acid (1 + 9). Filter the solution through an ashless paper of fine porosity in a stainless steel, silver, or platinum funnel and into a platinum dish. Wash the filter five times with water. Continue as described under separation of silica, beginning with the addition of 5 ml. of acetic acid (1 + 2).

PHOSPHATE ROCK. Fuse a 0.5000-gram sample with sodium hydroxide, and disintegrate the melt as described for cryolite and fluorspar. Wash out the crucible with a jet of hot water, then with dilute hydrochloric acid (1 + 20). Cool the solution, dilute to 200 ml., and neutralize with concentrated hydrochloric acid. Add the acid dropwise and stir the solution to prevent excessive localized concentration of acid. Add only 1 to 2 ml. of acid in excess of that required to dissolve the precipitated phosphate and hydroxides. Dissolve 0.5 gram of boric acid in the solution. Dilute to 500 ml. in a volumetric flask, and transfer a 50-ml. aliquot to a 300-ml. platinum dish containing a solution of about 2.8 grams (20 pellets) of sodium hydroxide in 120 ml. of water. Continue as described for the determination of silica.

In the precipitation of silica from phosphate rock and other phosphate-containing materials, the precipitate is a mixture of the oxine salts of molybdisilicic and molybdiphosphoric acids. To obtain the weight of the silica salt, the phosphorus pentoxide content of the original sample is determined by a standard volumetric method (11) and the equivalent weight of the oxine salt of molybdiphosphoric acid is subtracted from the weight of the precipitate.

MISCELLANEOUS SILICEOUS COMPOUNDS CONTAMINATED WITH FLUORIDES AND PHOSPHATES. The method for phosphate rock may be applied to a variety of samples decomposable by a sodium hydroxide fusion when the following precautions are observed:

The weight of the sample should not exceed 0.25 gram. Sufficient boric acid must be added to complex the fluorine. The aliquot taken for the precipitation of silica must not contain more than 30 mg. of silica plus phosphorus pentoxide.

Separation of Silica. Add 8 drops of thymol blue indicator, then concentrated hydrochloric acid, dropwise, until the color changes from yellow to red. Successively add 8 ml. of hydrochloric acid (1 + 9), 5 ml. of acetic acid (1 + 2), and 20 ml. of 10% ammonium molybdate solution. Stir the solution between additions of reagents and stir vigorously for 1 minute after the addition of the molybdate reagent. Allow 15 minutes for the formation of molybdisilicic acid.

Add 40 ml. of hydrochloric acid (1 + 1), and precipitate the silica immediately by adding 60 ml. of 8-hydroxyquinoline solution from a buret, stirring constantly during the addition. Cover the dish, and heat it in a water bath at 60° C. for 10 minutes, stirring occasionally.

Cool to room temperature in a water bath, allow the precipitate to settle, and filter through a weighed porcelain filtering crucible. Transfer all the liquid before washing is begun. Wash twice by decantation with 25-ml. portions of wash solution and transfer the precipitate to the crucible. Police the beaker thoroughly with the wash solution and wash the precipitate with the wash solution 10 times after the transfer has been completed. Wash once with 5 ml. of water. Dry the precipitate 1 hour at 140° C.

Cover the hot crucible with a watch glass, and cool the precipitate for 30 minutes in an evacuated desiccator. Weigh rapidly to eliminate errors from absorption of moisture. Use more than one desiccator when a large number of samples are to be weighed. Subtract a blank representing the weight of precipitate obtained by carrying equal quantites of all the reagents through the steps of the procedure.

Calculations. For samples containing phosphate

$$\text{Net weight of ppt.} - \frac{\text{weight of P}_2\text{O}_5 \text{ in sample}}{0.03174} =$$

weight of oxine salt of molybdisilicic acid

Weight of oxine salt of molybdisilicic acid $\times$ 0.02510 = weight of SiO$_2$.

For samples free of phosphate net weight of ppt. $\times$ 0.02510 = weight of SiO$_2$

DEVELOPMENT OF THE METHODS

It was decided at the outset that two procedures would be required for the wide range of silica determinations. For materials of small silica content the logical method would be a photometric procedure based on the molybdisilicic acid or molybdenum-blue reactions. For materials of higher silica content either a volumetric or a gravimetric procedure appeared appropriate.

Photometric Procedure. Preliminary studies were hampered by the lack of silica-free reagents. All reagent-grade fluorides contained silica, and the existing methods for the determination of their silica content were inadequate for yielding correction factors. To obtain a suitable source of fluorine, reagent-grade hydrofluoric acid was redistilled in a platinum still by the method of Hoffman and Lundell (12).

Boric acid of exceptional purity is obtainable and was used for complexing the fluorine prior to application of either a photometric or volumetric method. Colorimetric methods for the determination of silica as molybdisilicic acid or molybdenum blue, as well as gravimetric methods for the separation of silica as the oxine or pyramidone salt of molybdisilicic acid, are dependent on the quantitative formation of molybdisilicic acid. A technique developed (4) for the formation of molybdisilicic acid was tested with various quantities of boric acid. Quantities up to 9 grams did not interfere with adjustment of the pH, but the full 9 grams sometimes led to precipitation of the acid in subsequent operations. Accordingly, 8 grams was set as the maximum quantity to be added.

A series of photometric determinations was made by the molybdenum blue method (4) with 8-gram additions of boric acid and additions of fluorine in 0.1-gram increments from 0.0 to 0.8 gram. Silica, in the form of sodium silicate, was added in 0.2-mg. increments from 0.0 through 1.0 mg. As 0.8 gram of fluorine did not interfere significantly with the silica determination, the technique was used for the evaluation of redistilled hydrofluoric acid for vapor pressure measurements (5).

The reproducibility of results by the photometric method is essentially the same (0.02 mg. of silica) in the presence of fluorine as in its absence (4).

Gravimetric Procedure. Preliminary studies showed that the volumetric method of Vasil'ev and Barinová (27) has an accuracy of about 2% when applied to samples free of phosphates. This accuracy was deemed inadequate for a method which would be complicated further by use of a correction factor for phosphorus. None of the other volumetric methods for silica (10, 20, 28-30) appeared to offer any advantage over the method of Vasil'ev and Barinova, although a greater accuracy was claimed for some.

Table I. Precision of Gravimetric Method in Optimum Range of Silica

Bureau of Standards No.	No. of Determinations	Silica Added, Mg.	Silica Found, Mg.		
			Average	Maximum	Minimum
Glass sand					
81	13	20.00	19.97	20.05	19.89
	4	10.00	9.99	10.02	9.95
Feldspar					
70	9	20.00	20.05	20.15	19.94
70	3	10.00	9.99	10.03	9.97
99[a]	6	20.60	20.57	20.69	20.47
	3	10.30	10.28	10.29	10.26

[a] Sample also contained 0.14% P$_2$O$_5$. Reported values corrected for coprecipitated phosphorus compound.

Table II. Effect of Added Fluorine on Determination of Silica in Feldspars

Bureau of Standards No.	HF Added, Gram	SiO$_2$, Mg.	
		Added	Found[a]
70	0.00	20.00	20.03
	0.80	20.00	20.05
99	0.00	20.60	20.53
	0.80	20.60	20.52

[a] Average of three analyses.

Because of its high molecular weight, the oxine salt of molybdisilicic acid is suited admirably for a gravimetric method when the proper conditions for precipitation, washing, and drying are defined. Among the variables expected to influence the precipitation were the amounts of ammonium molybdate and of oxine, and the pH when the oxine is added.

The amount of ammonium molybdate was set at 20 ml. of a 10% solution. Experiments showed this to be an adequate excess for 40 mg. of silica, whereas the quantity to be determined rarely would exceed 25 mg.

A large excess of oxine was necessary for quantitative separation of silica. Tests showed that 60 ml. of a 1.4% solution of oxine, required for 40 mg. of silica, were suitable for smaller amounts as well.

Molybdenum forms an insoluble salt with oxine in weakly acid solutions, and the solution of molybdisilicic acid must be made strongly acidic just prior to, or during, the addition of the oxine to prevent coprecipitation of such molybdenum-oxine compounds. Addition of 40 ml. of hydrochloric acid (1 + 1) was necessary to prevent contamination of the precipitate.

The solubility of the precipitate was recognized as appreciable. Various weights of precipitate were digested for 1 hour with 100 ml. of hydrochloric acid (1 + 9) and filtered. The weights of the residues from evaporation of the filtrates indicated that the solubility of the precipitate was 0.13 gram per 100 ml. The solubility was offset through the use of a wash solution consisting of a saturated solution of the salt in a mixture of hydrochloric and acetic acids in the same concentrations as in the precipitation medium.

Volynets (28) reported that the molecule of the oxine salt of molybdisilicic acid is composed of one mole of silica, twelve of molybdenum trioxide, and four of oxine. The ratios given by Volynets were approximated by following through the procedure proposed by him for the determination of silica. A known amount of silica was precipitated as the oxine salt. The precipitate was filtered but not washed. The excess oxine in the filtrate was determined volumetrically, and the portion in the precipitate was calculated. The residue of silica and molybdenum trioxide was weighed after it had been ignited to remove the oxine.

The gravimetric method of Volynets (28) was unsuited to the present problem because even if the ashing conditions could be controlled to prevent loss of molybdenum trioxide, the method would not be applicable in the presence of phosphorus.

From the work of Illingworth and Keggin (*13*) on the salts of the heteropoly acids and of Berg (*2*) and Scharrer (*22*) on the oxine salt of molybdiphosphoric acid, it appeared probable that the oxine salt of molybdisilicic acid would be a hydrate. Portions of the silica salt were dried to virtually constant weight in a vacuum desiccator over Drierite and then were heated to constant weight at 70°, 105°, and 140° C. The total loss in weight on heating was 1.1% or the approximate equivalent of 1.5 molecules of water. These tests and others demonstrated that drying at a temperature of 140° C. for 1 hour provided the best means of obtaining a reproducible weight in a reasonable time.

To establish a gravimetric factor, the percentage of silica in the molecule was determined. An indirect method appeared to offer greater accuracy than a direct gravimetric determination of the silica in a great preponderance of molybdenum salts and oxine.

Standard solutions of silica were prepared, just prior to use, by fusing 0.25-gram portions of Bureau of Standards glass sand 81 with a mixture of potassium carbonate and boric oxide. The melt was disintegrated in 200 ml. of hot water in a platinum dish. The resultant solution was cooled, just neutralized with hydrochloric acid, and diluted. Aliquots representing 10 and 20 mg. of silica were analyzed. Similar tests were made with Bureau of Standards feldspars 70 and 99 as sources of silica. The weight of the dried precipitates, corrected on the basis of a blank determination on an equivalent quantity of reagents, was divided into the weight of silica taken for analysis to obtain the factor. The results of 38 determinations were averaged to obtain the factor 0.02510, after calculations showed that no result should be excluded mathematically (*18*). The average deviation from the mean was 0.00007 and the maximum 0.00019.

The data from which the factor was calculated, Table I, show the precision of the method in the optimum range of silica.

A definite quantity of silica was determined in the presence of various quantities of fluorine. Hydrofluoric acid in quantities up to 0.8 gram did not affect the accuracy of the determination, provided 8 grams of boric acid were present (Table II).

The range of the gravimetric method desirably should overlap that of the photometric method (0.0 to 1.0 mg. of silica). Table III shows a series of determinations of small amounts of silica both with and without fluorine additions.

Because orthophosphoric acid reacts with ammonium molybdate to form the heteropoly acid which, in turn, reacts with oxine to form a precipitate analogous to the oxine–molybdisilicic acid salt, it was necessary to determine the gravimetric factor for the phosphorus compound, so that a correction could be made when phosphorus and silica were precipitated together.

The procedure would be complicated by an effort to offset the respective solubilities of the phosphate and silica salts by use of more than one wash solution or of a mixed wash solution. In initial tests, therefore, the phosphate precipitate was washed with the silica wash solution. Various amounts of phosphorus pentoxide were added as orthophosphoric acid and precipitated. The precipitates were washed and dried in the same manner as the silica salt. The results appeared reasonable, although the weights of precipitate from small amounts of phosphate were higher proportionately than those from large amounts of phosphate, an indication that some factor other than solubility was affecting the results.

When mixtures of a fixed amount of silica with various increments of phosphate were analyzed, the increase in weight of precipitate due to the phosphate salt was remarkably linear in relation to the phosphate addition. The weight of precipitate attributable to phosphate was not so great as when the phosphorus was precipitated alone and washed with the silica wash solution. The explanation apparently lay in an equilibrium between the precipitate on the filter and the wash solution. When the phosphate salt alone was washed with the silica wash solution, some dissolved and was replaced by an equivalent quantity of the

silica salt. The result was a net increase in weight, as the silica salt contains 4 moles of oxine to 3 for the phosphate compound. When phosphate and silica were precipitated together, the silica salt protected the phosphate compound from contact with the wash solution and stabilized the system.

In the determination of the phosphate factor, Bureau of Standards phosphate rock samples 56a and 120 were the source of phosphorus. Twelve 1-gram samples were digested with perchloric acid and filtered, and aliquots of about 20 mg. of phosphorus pentoxide were analyzed, along with a known amount of silica. The weight of the silica salt was subtracted from the weight of the combined precipitates to obtain the weight of the phosphate salt. The weight of the phosphate salt then was divided into the weight of added phosphorus pentoxide to obtain the factor. Eleven of the results were averaged to obtain the factor, 0.03174. The average deviation from the mean was 0.00003 and the maximum deviation 0.00007.

To test the validity of the factor, mixtures of silica and phosphoric acid were analyzed. The theoretical value for weight of the phosphate precipitate was subtracted from the total weight of precipitate, and the weight of silica was calculated from the difference. Typical results in Table IV indicate that the correction factor is satisfactory.

Other tests showed that fluorine in amounts equivalent to as much as 0.8 gram of hydrogen fluoride was without effect on the accuracy of the method with samples containing phosphates, provided 8 grams of boric acid were present.

Germanium (*1*) and arsenic (*22*) in groups IV and V, respectively, are known to react with ammonium molybdate and oxine to form precipitates. These elements and others in their groups were tested for interference by subjecting the equivalent of 10 mg. of their oxides to the conditions used for the analysis of silica. Table V gives the results of the tests.

Table V shows that compounds of tetravalent germanium and of pentavalent vanadium and arsenic interfere by forming compounds analogous to those of silicon and pentavalent phosphorus. The precipitates from compounds of trivalent phosphorus and arsenic do not form until the strongly acid solutions containing

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Table III. Accuracy of Gravimetric Method in Determination of Small Quantities of Silica

SiO_2 Added, Mg.	HF Added, Gram	SiO_2 Found, Mg.
0.50	0.00	0.51
0.50	0.00	0.49
0.50	0.80	0.50
1.00	0.00	0.99
1.00	0.00	0.99
1.00	0.80	1.01
2.00	0.00	2.00
2.00	0.00	1.99
2.00	0.80	2.02

Table IV. Accuracy of Gravimetric Method Applied to Synthetic Samples Containing Phosphorus

Added, Mg.		Weight of Oxine Precipitate, Gram			SiO_2 Found, Mg.
SiO_2	P_2O_5	Total[a]	P_2O_5 (Calcd.)	SiO_2	
10.00	0.00	0.3991	0.0000	0.3991	10.02
10.00	1.00	0.4317	0.0315	0.4002	10.05
10.00	2.00	0.4633	0.0630	0.4003	10.05
10.00	3.00	0.4925	0.0945	0.3980	9.99
10.00	4.00	0.5270	0.1260	0.4010	10.07
10.00	5.00	0.5564	0.1575	0.3989	10.01
20.00	0.00	0.7990	0.0000	0.7990	20.05
20.00	1.00	0.8319	0.0315	0.8004	20.09
20.00	2.00	0.8637	0.0630	0.8007	20.10
20.00	3.00	0.8933	0.0945	0.7988	20.05
20.00	4.00	0.9256	0.1260	0.7996	20.07
20.00	5.00	0.9570	0.1575	0.7995	20.07
10.00	0.00	0.3963	0.0000	0.3963	9.95
10.00	5.00	0.5560	0.1575	0.3985	10.00
10.00	10.00	0.7140	0.3151	0.3989	10.01
10.00	15.00	0.8696	0.4726	0.3970	9.96
10.00	20.00	1.0303	0.6301	0.4002	10.05
10.00	25.00	1.1882	0.7876	0.4006	10.06

[a] Corrected for blank on reagents.

Table V. Tests of Possible Interfering Elements from Groups IV and V

Element	Added as	Forms Ppt.
Titanium	TiCl₄	Yes[a]
Germanium	GeCl₄	Yes
Zirconium	ZrCl₄	Yes[a]
Tin	SnCl₂.2H₂O	No
	SnCl₄.5H₂O	No
Lead	Pb(NO₃)₂	No
Thorium	Th(NO₃)₄.12H₂O	No
Phosphorus	Na₂HPO₃.5H₂O	Yes
	Na₃PO₄	Yes
Vanadium	NH₄VO₃	Yes
Arsenic	Na₂HAsO₃	Yes
	H₃AsO₄	Yes
Antimony	SbCl₃	No
	K₂H₂Sb₂O₇.4H₂O	No
Bismuth	BiCl₃	No
	NaBiO₃	No[b]

[a] Hydrolysis, with resultant precipitation, occurred when samples were heated.
[b] Decomposed, on acidification, with liberation of chlorine.

oxine have been digested at 60° C. It is recommended that the method not be applied to samples containing arsenic and only to those samples in which the phosphorus is in the pentavalent state. Phosphorus and silicon probably could be separated from zirconium and titanium in an alkaline medium if necessary.

The preparation of fluorides for analysis was limited to alkaline decomposition techniques because of the volatility of silicon tetrafluoride. Fusion of the sample with sodium hydroxide in a nickel or silver crucible has the advantage of simplicity and speed and has been used successfully for the decomposition of siliceous materials in which the silica was later determined by the conventional gravimetric method. Virtually all samples decomposed by this method left a slight insoluble residue as a result of particles of the original material being blown either to the sides or the lid of the crucible. This difficulty was obviated by adding a few drops of alcohol to wet the individual particles with an alcoholic solution of sodium hydroxide (15).

Other methods for solution of the sample included fusions with sodium carbonate alone, sodium carbonate with boric oxide (4), and sodium carbonate with potassium carbonate. The melts disintegrated slowly in water and usually precipitated gelatinous silica on acidification. The most satisfactory method of decomposition with respect to time, disintegration of the melt, and complete solubilization of silica was a fusion with potassium carbonate and boric oxide in a platinum dish. Widely varying weights of a precipitate that contained 1 mole of oxine to 6 moles of molybdic oxide were obtained in blank determinations on large quantities of potassium carbonate. The precipitate formed only when a large amount of carbonate was left in solution prior to the addition of the molybdate and oxine. The potassium carbonate-boric oxide fusion can be applied to samples high in silica, such as glass sand and the feldspars. The melts are disintegrated in water and then made acidic. Much of the carbon dioxide escapes, and the remainder is diluted to innocuity. This fusion should not be used for the analysis of samples such as fluorspar or cryolite where the entire melt is used for analysis.

Silver, removed from the crucibles by the scouring action of the fusions, reacted with ammonium molybdate or the molybdiacids to form molybdenum blue. Filtration removed the silver, but some silica remained on the filter. This silica can be recovered by an additional fusion should the accuracy justify the additional time. The error introduced by filtration of the silver is detectable only where silica is a major constituent of the sample.

APPLICATION TO SODIUM FLUOSILICATE. Among the products that might be expected from the recovery of by-product fluorine are sodium fluosilicate, calcium fluoride, and synthetic cryolite. Analyses of sodium fluosilicate were made upon 0.1-gram samples that were dissolved directly in a dilute solution of sodium hy-

droxide in a platinum dish. Nine analyses gave an average of 31.58% of silica, a maximum of 31.71%, and a minimum of 31.47%, as compared with a theoretical value of 31.94%.

APPLICATION TO CALCIUM FLUORIDE. Table VI shows the results of application of the method to Bureau of Standards fluorspar 79. The certified silica content of the sample, 1.88%, was obtained by averaging the results of 15 collaborators whose reported results varied from 1.70 to 1.96%. The certified value is believed by the Bureau of Standards to be accurate within ±0.15%.

APPLICATION TO CRYOLITE. The applicability of the method to the analysis of cryolite was tested with a sample of Greenland cryolite which, by spectrographic analysis, contained less than 0.01% silica. Bureau of Standards bauxite sample 69 was added to simulate samples of higher silica content. Results of the tests, Table VII, indicate that the method is adequate for the analysis of cryolite.

APPLICATION TO OPAL GLASS. Bureau of Standards opal glass 91, which contains 67.5% silica and 5.7% fluorine, yielded erratic results when first analyzed. After development of the sodium hydroxide fusion technique specified above, however, 16 analyses, in which 0.2500-gram samples were decomposed, diluted and aliquoted, yielded an average of 16.74 mg., a maximum of 16.88 mg., and a minimum of 16.53 mg. of silica as compared with 16.88 mg. taken. The slightly low results were traceable to incomplete decomposition of the sample.

APPLICATION TO PHOSPHATE ROCK. The most rigorous test of the method was in the analysis of multiple samples of Bureau of Standards phosphate rocks for phosphorus and silica, correcting for the phosphorus, and calculating the percentage of silica (Table VIII).

Table VI. Accuracy of Gravimetric Method in Analysis of Fluorspar

Sample Wt., Gram	SiO₂ Found, %[a]		
	Average	Maximum	Minimum
0.1500	2.00	2.03	1.97
0.2500	2.01	2.02	1.97
0.5000	2.01	2.03	1.98

[a] Each set of values is result of four determinations. Bureau of Standards value, 1.88%.

Table VII. Accuracy of Gravimetric Method in Analysis of Cryolite with Known Additions of Silica

Sample	SiO₂ Taken, %	SiO₂ Found, %[a]		
		Average	Maximum	Minimum
Cryolite, 0.5 g., bauxite 0.05 g.	0.63	0.63	0.66	0.61
Cryolite, 0.5 g., bauxite 0.1 g.	1.26	1.25	1.26	1.23

[a] Each set of values is result of six determinations.

Table VIII. Accuracy of Method in Analysis of Phosphate Rock

Bureau of Standards No.	No. of Determinations	Bureau of Standards Value for SiO₂, %	SiO₂ Found, %		
			Average	Maximum	Minimum
56a	9	11.01[a]	10.91	11.27	10.52
120	10	7.6[b]	7.81	8.02	7.49

[a] Average of four values ranging from 10.60 to 11.50. Work by bureau indicates that an uncertainty of at least ±0.2% should be assigned to this value.
[b] Work by bureau indicates that recorded value, rather than average value of 7.40 obtained from three results ranging from 7.03 to 7.70, represents more nearly true silica content of sample. An uncertainty of at least ±0.2% should be assigned to tabulated value.

PRECISION AND ACCURACY. The accuracy of the method is not the same for all materials. Small portions of refractory fluoride samples sometimes do not react with the flux. This source of error does not occur in the analysis of readily soluble compounds, such as sodium fluosilicate.

Deviations from the mean not exceeding 0.15 mg. of silica should be expected in a series of analyses of sodium fluosilicate, fluorspar, or cryolite. The accuracy of the method probably is as good as the precision, although the percentage accuracy of the silica determination in cryolite and fluorspar suffers somewhat from limitations in the size of sample that can be used.

Table IX. Precision of Gravimetric Method Applied to Various Materials

Sample	No. of Analyses	Average SiO₂ Found, %	Probable Error Single determination, of SiO₂	Parts per thousand
Sodium fluosilicate	9	31.58	0.06	2
Fluorspar 79	12	2.01	0.01	5
Cryolite + bauxite 69	6	1.25	0.01	8
Opal glass 91	16	16.74[a]	0.02[a]	1
Phosphate rock 56a	9	10.91	0.18	17
Phosphate rock 120	10	7.81	0.12	15

[a] Reported as milligrams of silica per determination.

The silica content of sodium fluosilicate, as determined by the method, is lower than the theoretical value. The experimental value is believed to be near the actual silica content, however, as the best reagents contain contaminants sufficient to account for the difference. The experimentally determined silica content of the fluorspar, although higher than the certified value, is within the limit of accuracy claimed by the Bureau of Standards. The higher values are considered to be closer to the true silica content, as the fluorspar did not contain sufficient foreign elements to cause a significant error through the formation of oxine salts of their molybdi- acid analogs of the silica complex. Spectrographic analyses of the precipitates established the absence of significant amounts of contaminants, such as calcium.

The results for silica in phosphate rock are included to show the effectiveness of the method under extreme conditions. On the whole, the accuracy is rather remarkable when it is considered that the silica result was obtained indirectly.

The precision of the gravimetric method was demonstrated further by calculation of the probable error of a single determination (18) for the various experimental materials (Table IX).

STRUCTURE AND COMPOSITION OF THE PRECIPITATE. X-ray diffraction patterns showed that the oxine salts of both molybdisilicic and molybdiphosphoric acids were unchanged by heating to 140° C. The existence of at least three crystalline modifications of the oxine salt of molybdisilicic acid was indicated by the diffraction patterns. The first was the precipitate formed by rapid addition of oxine to cold molybdisilicic acid. The second was the recrystallized compound that is filtered and weighed. A third modification was the crystalline precipitate that separated from the saturated wash solution on cooling.

Typical samples of the oxine salt of molybdisilicic acid were studied by optical and electron microscopy. Crystals of the precipitate that was weighed were triclinic, pinacoidal class. The form appeared to be normal for precipitates obtained under the conditions of the analytical method. The crystals were biaxially negative, $Bx_a = X$, with moderate to strong birefringence. All the indexes of refraction were above 1.70. Optic axial angle $2V$ was 15° to 20°. The crystals ranged in size from 0.2 to 1.0 micron in length and from 0.1 to 0.5 micron in width. The microscopic observations, in accord with the x-ray patterns, showed that the crystals were unaltered by heating to 140° C.

Crystals separating from the saturated wash solution also were triclinic, pinacoidal class, and varied in size from rhombs 20 microns on edge to rods and tablets 200 microns in length. The crystal habits and the interfacial-angle measurements of these crystals were the same as those for the crystals which were weighed.

The freshly precipitated oxine salt before digestion at 60° C. consisted of crystals that were poorly developed and smaller than the ones that were later filtered and weighed. The initial crystals underwent a transformation during the digestion.

Volynets (28), in assigning the ratios of silica, molybdenum trioxide, and oxine to the oxine salt of molybdisilicic acid, did not give the formula. Although the significance of the formula is primarily theoretical, provided a volumetric method or the gravimetric method of Volynets is used, the formula is of value in confirming the gravimetric factor determined in the present study.

The structural stability of the oxine salt of molybdisilicic acid, as found by both x-ray and microscopic methods, is evidence that the loss on drying to constant weight at 140° C. represents adsorbed moisture and not water of constitution. It was assumed at first, by analogy with the reported formula (2) for the oxine salt of molybdiphosphoric acid, $3(C_9H_7ON).H_7[P(Mo_2O_7)_6].2H_2O$, that the silica compound which was weighed was a stable hydrate. If the empirically determined gravimetric factor of 0.02510 is correct, however, and it is believed so within 0.5%, an anhydrous compound of oxine and molybdisilicic acid, $4C_9H_7ON.$ $H_4SiMo_{12}O_{40}$, with a theoretical silica factor of 0.02498 is indicated. This formula is analogous to that reported by Alimarin and Alekseeva (1) for the germanium salt.

Berg (2), in assigning the formula, $3C_9H_7ON.H_7[P(Mo_2O_7)]_6.$-$2H_2O$, to the oxine salt of molybdiphosphoric acid, stated that the theoretical factor for phosphorus pentoxide should be 0.0305. Scharrer (22) analyzed portions of the precipitate, dried to constant weight at 105° C., by the method of Lorenz (17) and found 3.063% phosphorus pentoxide. Because the precipitation technique in the present study differs from that of Scharrer in details, the results of the two studies may not be strictly comparable. The precipitates contained, on the basis of the added phosphate, 3.174% phosphorus pentoxide. If the phosphorus precipitate were dissolved slightly by the wash solution, 3.1395%, the theoretical value for the compound $3C_9H_7ON.H_3PMo_{12}O_{40}$, well could represent the actual phosphorus pentoxide content of the precipitate.

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Spectroscopic Determination of Cyclopentadiene and Methylcyclopentadiene

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An ultraviolet spectroscopic method is described for determining cyclopentadiene and methylcyclopentadiene in the presence of each other. The sample for analysis is first depolymerized by passing it through a heated tube to convert the cyclopentadiene and methylcyclopentadiene to the monomeric form. The ultraviolet absorption of the depolymerized sample is determined at two different wave lengths, from which the composition of the sample is calculated. Aromatic hydrocarbons and conjugated diolefins interfere. However, by dimerizing the sample, the cyclopentadiene and methylcyclopentadiene are converted to dimers which have little ultraviolet absorption, and a blank ultraviolet absorption value is obtained which corrects for these interferences, if the concentration of interferences is small compared to the concentrations of cyclopentadiene and methylcyclopentadiene.

THE ultraviolet absorption spectrum of cyclopentadiene has been determined by Pickett, Paddock, and Sackter (3), but the literature gives no method for determining cyclopentadiene by ultraviolet spectroscopy, and no data on the ultraviolet absorption of methylcyclopentadiene. The authors postulated that there would be a shift in the ultraviolet absorption peak of methylcyclopentadiene to a higher wave length than the peak for cyclopentadiene and proof of this was undertaken.

Pure cyclopentadiene and methylcyclopentadiene were separated from hydrocarbon fractions containing these compounds produced by the thermal cracking of petroleum. It was indicated that the methylcyclopentadiene obtained was the 1-methyl- and 2-methylcyclo-1,3-pentadiene isomers (1). The physical constants of the cyclopentadiene were: boiling point, 41° C.; $d_4^{20} = 0.7982$; and $n_D^{20} = 1.4465$. The physical constants of the methyl cyclopentadiene were: boiling point, 73° C.; $d_4^{20} = 0.8112$; and $n_D^{20} = 1.4509$. The ultraviolet absorption spectra of the cyclopentadiene and methylcyclopentadiene and the spectra of their dimers were determined. The spectra obtained are given in Figure 1.

It will be observed that the absorption peak for cyclopentadiene is at 240 mμ and that for methylcyclopentadiene at 247 mμ, and that the absorption by their dimers is comparatively very small. By making use of these differences in ultraviolet absorption, the following method was developed for determining cyclopentadiene and methylcyclopentadiene in the presence of each other.

REAGENTS

Iso-octane, Eastman technical grade. Activated silica gel, 28- to 200-mesh (2).

APPARATUS

Beckman quartz photoelectric spectrophotometer equipped for ultraviolet spectroscopy. Silica gel column. Depolymerization apparatus (4). Volumetric flasks, 50- and 100-ml. Pipets, 5-, 10-, 15-, and 25-ml.

PROCEDURE

Purification of Iso-octane. Pass the iso-octane repeatedly through the silica gel column until it shows no absorption at 240 mμ. Iso-octane which has been used in the analysis can be reclaimed by silica gel treatment.

Preparation of Sample. If aromatics or conjugated diolefins other than cyclopentadiene and methylcyclopentadiene are present and the cyclopentadiene and methylcyclopentadiene are not all in the dimeric form, heat the sample to 100° C. for 6 hours in a closed container capable of withstanding a pressure of 10 atmospheres. This operation is performed to prepare a blank sample for determining the ultraviolet absorption of the interferences in the sample, inasmuch as the dimers of cyclopentadiene and methylcyclopentadiene have no absorption at the wave lengths used; it is not necessary if neither of these conditions exists.

Pipet approximately 5 ml. of sample into a tared 100-ml. volumetric flask and weigh. Dilute to the mark with iso-octane. Place the outlet tube of the depolymerization apparatus in a 100-ml. volumetric flask containing about 30 ml. of iso-octane. Cool the flask in an acetone–dry ice bath. Adjust the power input to the depolymerization apparatus in order to have the depolymerized sample vapor leave the heating coil at 340° to 360° C. This is accomplished by predetermining the setting of a variable voltage transformer to give the above temperature of vapors immediately leaving the heating coil as indicated by a test thermocouple inserted within the depolymerization tube. Transfer 5 ml. of the diluted sample into the funnel at the top of the depolymerization apparatus. When the funnel is empty, add 5 ml. of iso-octane to the funnel, washing down the sides during the addition. Remove

the volumetric flask from the acetone–dry ice bath, allow it to come to room temperature, and dilute to the mark with iso-octane. Dilute a portion of the contents according to the following table:

Wt. % of Cyclopentadiene Plus Methyl Cyclopentadiene in Sample	Dilutions	
	1st	2nd
82–100	5/100	5/50
28–89	5/100	10/50
11–33	5/100	25/50
6–17	5/100	...
3–8	5/50	...
0–3	15/50	...

Ultraviolet Absorption. Prepare a blank reference sample by diluting the dimerized sample if dimerization were performed to the same degree as was done for the depolymerized sample. With the spectrophotometer, determine the optical density of the depolymerized diluted sample at 240 and 258 mμ with the spectrophotometer set at 100% transmittance on the blank diluted sample at each wave length. If the sample contains no interferences and dimerization was not performed, use a blank of iso-octane.

Calculations. Calculate the extinction coefficients from the optical densities observed at the two wave lengths, using the following equation:

$$K = \frac{D}{CL}$$

where
K = extinction coefficient
D = optical density
C = concentration of sample in grams per liter of solution
L = optical path in cm.
making
K_1 = extinction coefficient at 240 mμ
K_2 = extinction coefficient at 258 mμ

Calculate the weight per cent of the cyclopentadiene and methylcyclopentadiene from the two equations:
X = weight % of cyclopentadiene = $100 (k_1K_1 - k_2K_2)$
Y = weight % of methyl cyclopentadiene = $100 (k_3K_2 - k_4K_1)$

Determine the constants k_1, k_2, k_3, and k_4 in these equations by carrying out the above procedure, using pure cyclopentadiene and. methylcyclopentadiene dimers separately for the cracking treatment, determining the extinction coefficients for the two monomers, and substituting these values in the following equations:

$$k_1 = K_dA$$
$$k_2 = K_bA$$
$$k_3 = K_aA$$
$$k_4 = K_cA$$

where
$$A = \frac{1}{K_aK_d - K_bK_c}$$
K_a = extinction coefficient of cyclopentadiene at 240 mμ
K_b = extinction coefficient of methylcyclopentadiene at 240 mμ
K_c = extinction coefficient of cyclopentadiene at 258 mμ
K_d = extinction coefficient of methylcyclopentadiene at 258 mμ

Table I. Results of Analysis of Synthetic Samples of Mixtures of Cyclopentadiene and Methylcyclopentadiene

Cyclopentadiene		Methylcyclopentadiene	
Present, wt. %	Found, wt. %	Present, wt. %	Found, wt. %
90.8	89.3	9.2	8.5
31.7	31.3	68.3	69.2
57.9	58.3	42.1	43.3

ACCURACY OF METHOD

The results of a series of analyses on synthetic samples containing both compounds in known concentrations are given in Table I. As indicated, the widest deviation from the actual percentage present is 1.5%.

Most other compounds that would be present in a hydrocarbon fraction containing cyclopentadiene and methylcyclopentadiene do not interfere appreciably. Cyclopentadiene and methyl-cyclopentadiene have extinction coefficients at 240 mμ of approxi-

mately 49 and 36 and at 258 mμ of 17 and 28, respectively. Aromatics have extinction coefficients below 3 at these wave lengths, and their interference is eliminated by using a reference blank of the material dimerized to convert the cyclopentadiene and methylcyclopentadiene to the dimers that have negligible absorption. Indene, however, has extinction coefficients at 240 and 258 mμ of 57 and 49, respectively, and, therefore, presents a definite interference if present in considerable quantity. If indene is present to any extent, it should be removed by fractional distillation.
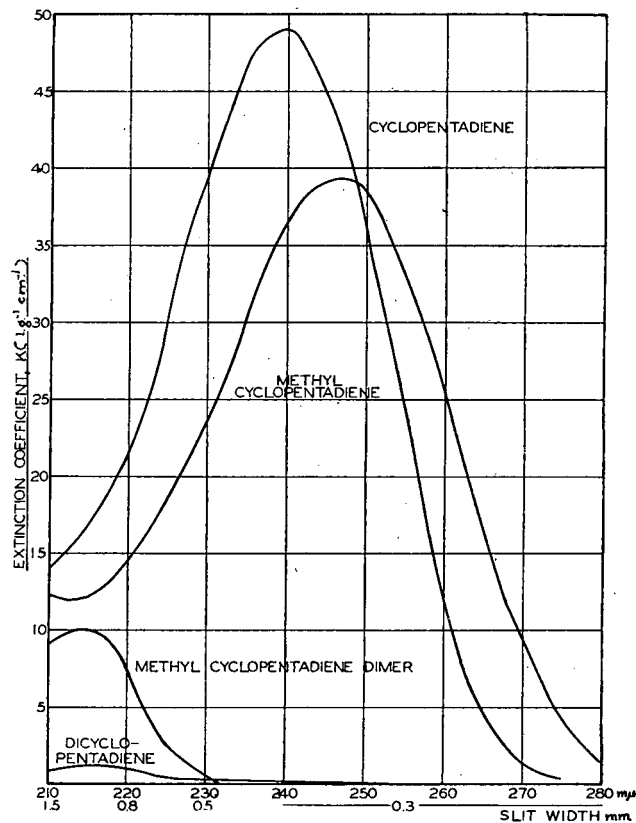

Figure 1. Ultraviolet Absorption Spectra of Cyclopentadiene, Methylcyclopentadiene, and Their Dimers

Other diolefins may interfere if present in large quantity but the blank absorption determined on the dimerized sample will minimize this interference. They may also cross-polymerize during the dimerization with cyclopentadiene and methylcyclopentadiene and not decompose during the subsequent depolymerization, thus causing an error in the analysis.

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Determination of Thiophene, Carbon Oxysulfide, and Carbon Disulfide in Producer Gas

A Spectrophotometric Method

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A simple, rapid method is presented by which the individual concentrations of carbon disulfide, carbon oxysulfide, and thiophene in a gas may be determined. Thiophene is quantitatively removed from a gas sample by scrubbing it with a piperidine-ethanol solution, and carbon oxysulfide and carbon disulfide are removed by solution as piperidine oxythiocarbamate and piperidine dithiocarbamate. Concentrations of thiophene and the piperidine carbamates are determined spectrophotometrically.

THE need for a rapid, simple method for the determination of organic sulfur in producer gas has long been recognized. Recently this need has expanded rapidly, paralleling closely the use of catalysts susceptible to sulfur poisoning, such as those employed in the Fischer-Tropsch process for the production of synthetic fuels, and the attendant need of developing scrubbers for removing sulfur compounds.

The organic sulfur compounds present in the gas are believed to consist almost entirely of mercaptans (thiols), thiophene, carbon disulfide, and carbon oxysulfide. Methods for the determination of some or all of these constituents have been described by Hutchison (1), Kemper and Guernsey (2), Oldach and Field (5), MacHattie and McNiven (3), Martin, Rueck, Knaggs, and Hakewill (4), Riesz and Wohlberg (6), and Shaw (7). Of all the compounds present only the mercaptans can be determined directly by absorption and analysis of the absorbing solution. The others have heretofore been determined indirectly by scrubbing the gas with suitable selective absorbents and estimating the residual sulfur content of the gas by burning it and absorbing the sulfur oxides formed. Obviously such a procedure is time-consuming and has other serious limitations that restrict its usefulness.

This paper presents a simple, rapid method of analysis which makes it possible to determine the individual concentrations of carbon disulfide, carbon oxysulfide, and thiophene in a gas. The minimal amount of sulfur that is conveniently evaluated by this method is 0.013 grain per 100 cubic feet of gas, which is equal to 0.0002 mg. of sulfur per liter.

The determination is based on the observations that thiophene is quantitatively removed from a gas sample by scrubbing it with a piperidine-ethanol solution and that carbon oxysulfide and carbon disulfide are effectively removed from the gas by solution as piperidine oxythiocarbamate and piperidine dithiocarbamate, respectively. The thiophene and the piperidine carbamates absorb strongly in the ultraviolet portion of the spectrum, and it is therefore possible to determine their concentrations spectrophotometrically. Spectrophotometric measurements are conveniently made with a Beckman model DU quartz spectrophotometer equipped with ultraviolet accessories.

The transmittance of any component of a solution is expressed mathematically as

$$\log_{10} \frac{T_0}{T} = ecx = d \qquad (1)$$

where T is the transmission of the component, e is its extinction coefficient, c is its concentration, x is the length of the optical path through the sample, and d is its optical density. It follows that the transmittance of all components of a solution can be expressed as

$$D = d_1 + d_2 + d_3 + \ldots\ldots d_n \qquad (2)$$

where D is the optical density of the solution and d_n is the optical density of the nth component. In general, n such equations, one for each of n selected spectral positions, are required to determine the concentration of each component present.
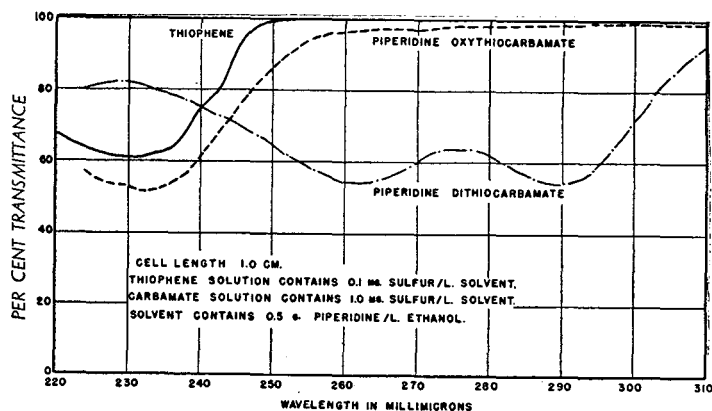

Figure 1. Ultraviolet Spectrograms of Thiophene, Piperidine Oxythiocarbamate, and Piperidine Dithiocarbamate

The wave lengths chosen for the analysis of organic sulfur in producer gas are 230, 240, and 290 mμ. At 290 mμ piperidine dithiocarbamate absorbs strongly, whereas both thiophene and piperidine oxythiocarbamate are relatively transparent, as shown in Figure 1.

An inspection of Figure 2, which reveals the ultraviolet spectrograms of benzene, toluene, ethylbenzene, and a mixture of the isomeric xylenes, the aromatic hydrocarbons most likely to occur in producer gas in small quantities, shows that these materials, while transparent at 290 mμ, absorb at 230 and 240 mμ. Therefore, a correction for their absorption is applied where necessary.

That ethanol and the piperidine-ethanol solution scrub benzene from the gas with equal facility is shown in Table I.

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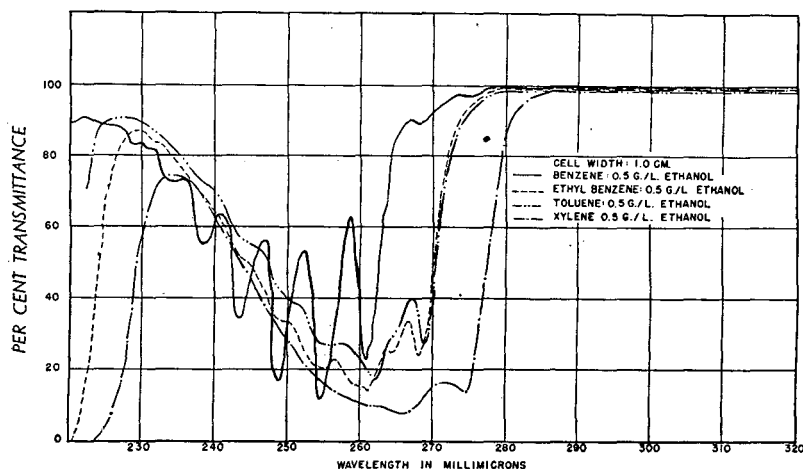
Figure 2. Ultraviolet Spectrograms of Benzene, Toluene, Ethylbenzene, and a Mixture of Isomeric Xylenes

using fresh 95% ethanol as the comparison standard. From the relationship;

$$D\lambda = D_{255} \frac{e\lambda}{e_{255}} \qquad (3)$$

the optical density at wave length λ is calculated. Here $D\lambda$ is the optical density of the piperidine-ethanol scrubbing liquor, at wave length λ (230 or 240 mμ), D_{255} is the optical density of the ethanol scrubbing liquor at 255 mμ, e_{255} is the extinction coefficient of benzene at the same wave length, and $e\lambda$ is the extinction coefficient of benzene at wave length λ. Because benzene is the principal aromatic present in producer gas, the error caused by ascribing all absorption from aromatics to benzene is insignificant. For most work the difference between the transmittances of ethanol and the piperidine-ethanol solution need not be considered.

PROCEDURE

Thiophene, Eastman grade, is purified to remove carbon disulfide as follows. One milliliter of piperidine, Eastman grade, is added to 50 ml. of thiophene. The product is then distilled through a fractionating column, and the
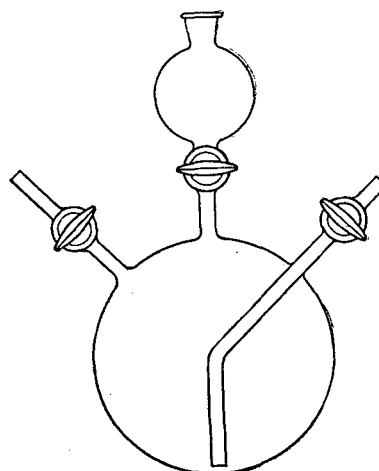
Table I. Removing Benzene from Producer Gas

Extraction	Dilution of Scrubbing Solution	Transmittance of Diluent at 255 mμ	Benzene, Mg. per Liter of Gas	Benzene Removed from Gas, %
Scrubbing Efficiency of Ethanol				
First	100–1	66.1	118	97.9
Second	None	41.1	2.5	96.8
Third	None	97.1	0.085	...
Scrubbing Efficiency of Piperidine-Ethanol Solution				
First	100–1	70.0	101.2	98.6
Second	None	63.1	1.3	100.0
Third	None	100.0	0.000	...

Table II. Scrubbing Efficiency of Piperidine-Ethanol Solution in Removing Thiophene from Gases

Extraction	Dilution of Solution	Transmittance of Diluent at 230 mμ	Sulfur, Mg. per Liter of Gas	Sulfur Removed from Gas, %
First	1000–1	55.0	30.20	98.4
Second	10–1	40.6	0.47	98.4
Third	None	86.1	0.008	100.0
Fourth	None	100.0	0.000	...

In making these tests a Tutweiler buret (Figure 3) was evacuated and a known amount of benzene vapor was added, after which the gas pressure was brought to atmospheric by adding carefully scrubbed producer gas. The scrubbing liquor was brought into intimate contact with the gas by shaking the buret for 3 minutes. At the end of that time the liquor was removed and the buret washed carefully with small successive portions of fresh liquor; the contact between gas and wash liquor was kept to a minimum. Washings and the scrubbing liquor were combined and the benzene concentration was determined spectrophotometrically. The operation was repeated until the spectrophotometer showed no benzene in the gas.

In Table II is portrayed the scrubbing efficiency of the piperidine-ethanol solution in removing thiophene from gases. Figure 4 demonstrates that alcoholic solutions of thiophene, carbon oxysulfide, and carbon disulfide are relatively transparent at 255 mμ; accordingly, no appreciable error is caused by ascribing all absorption at 255 mμ to aromatic hydrocarbons. In order to correct for the absorption of aromatic hydrocarbons at 230 and 240 mμ, respectively, the gas sample is scrubbed with 95% ethanol and its transmittance measured at 255 mμ,

Figure 3. Modified Tutweiler Buret for Determining Thiophene, Carbon Oxysulfide, and Carbon Disulfide in Producer Gas
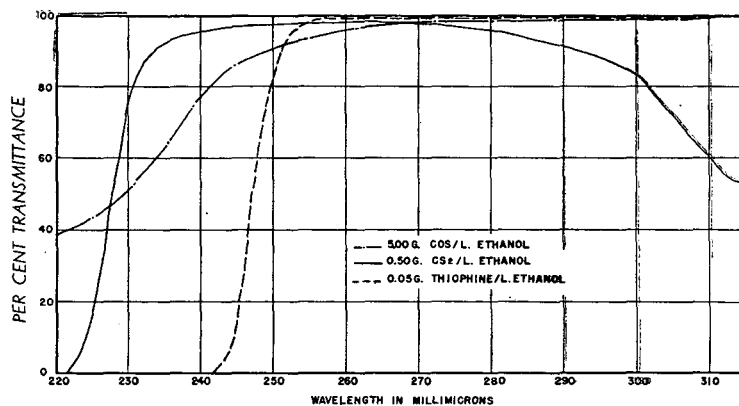

Figure 4. Ultraviolet Spectrograms of Carbon Disulfide, Carbon Oxysulfide, and Thiophene

forerunnings and tails are discarded. Piperidine dithiocarbamate is prepared by the reaction of piperidine with carbon disulfide in petroleum ether. The ether is removed by filtration through a sintered-glass funnel. The solid piperidine dithiocarbamate is washed several times with small amounts of petroleum ether, dried, and kept in a glass-stoppered bottle.

Piperidine oxythiocarbamate is made by reacting a saturated solution of potassium thiocyanate with 50% sulfuric acid, keeping the temperature of the reactants below 45° C. The gases evolved are scrubbed successively with a 30% potassium hydroxide solution and a solution containing 25% aniline and 75% ethanol. The carbon oxysulfide is then passed through ice and absorbed in a solution of piperidine and petroleum ether. The ether is removed by filtration. The precipitate, piperidine oxythiocarbamate, is washed several times with small portions of petroleum ether, dried, and kept in a glass-stoppered bottle. (Carbon oxysulfide is toxic.)

A piperidine-ethanol solution (0.5 gram of piperidine per liter of 95% ethanol) is prepared. It is stirred thoroughly in contact with air before it is used.

Solutions are made containing accurately weighed amounts of thiophene within the concentration range of 4 to 10 mg. of thiophene per liter of piperidine-ethanol solvent. Convenient concentrations are 4, 6, 8, and 10 mg., respectively.

Similar solutions of piperidine oxythiocarbamate and piperidine dithiocarbamate are prepared. All solutions are kept in glass-stoppered bottles. Because the carbamates decompose on standing, fresh reagents are prepared as required.

Solutions containing accurately weighed amounts of benzene in 95% ethanol are prepared and stored in glass-stoppered bottles. The solutions should contain approximately 0.1, 0.2, 0.3, and 0.5 gram of benzene per liter of ethanol.

The optical densities of the "standard" solutions of thiophene, piperidine oxythiocarbamate, piperidine dithiocarbamate, and benzene are determined at 230, 240, 255, and 290 mμ. From these measurements the extinction coefficients are ascertained.

Two gas samples, 1 liter each, are required for each analysis. Rubber connections are kept to a minimum between the sampling point and gas collection bottle. The rubber connections are boiled in 30% caustic before they are used. The Tutweiler buret (Figure 3), made from a 1-liter round-bottomed flask, a 60-cc. dropping funnel, and two stopcocks, is employed for scrubbing the gas sample. It is also recommended that a pair of such burets be used as gas-collecting bottles, thereby avoiding transfer of samples.

The gas sample is introduced into two clean Tutweiler burets. Twenty-five milliliters of 95% ethanol are added to the first buret and the gas sample is scrubbed with the alcohol by shaking the buret for 2 to 3 minutes. The scrubbing ethanol is then removed from the buret and its optical density is measured at 255 mμ, using ethanol as the reference standard. Twenty-five milliliters of the piperidine-ethanol solution are added to the second buret. After the gas has been scrubbed with this liquor by shaking the buret 2 or 3 minutes, the scrubbing liquor is removed and its transmittance is determined at 230, 240, and 290 mμ, piperidine-ethanol solution being employed as the reference standard.

The optical density of the piperidine-ethanol scrubbing liquor on a benzene-free basis is found, using the relationship

$$D\lambda = D_{255}\frac{e\lambda}{e_{255}} \tag{3}$$

and the equation

$$d_s = D - D\lambda \tag{4}$$

where D is the observed optical density of the piperidine-ethanol scrubbing liquor and d_s is its optical density on a benzene-free basis.

The concentrations of thiophene, carbon oxysulfide, and carbon disulfide are found by solving the following simultaneous equation

$$\begin{vmatrix} d_s = e_1c_1x + e_1'c_2x + e_1''c_3x \\ d_s' = e_2c_1x + e_2'c_2x + e_2''c_3x \\ D_3 = e_3c_1x + e_3'c_2x \end{vmatrix} \tag{5}$$

in which d_s is the optical density at 230 mμ corrected for benzene, d_s' is the corrected optical density at 240 mμ, D_3 is the optical density at 290 mμ; c_1, c_2, and c_3 are the concentrations of carbon disulfide as piperidine dithiocarbamate, carbon oxysulfide as piperidine oxythiocarbamate, and thiophene, respectively; e_1,

e_2, and e_3 are the extinction coefficients of piperidine dithiocarbamate at 230, 240, and 290 mμ; e_1', e_2', and e_3' are the extinction coefficients of piperidine oxythiocarbamate at the same wave lengths, respectively; and e_1'' and e_2'' are the extinction coefficients of thiophene at 230 and 240 mμ, respectively. The length of the optical path, in this case 1 cm., is designated by x.

Repeated tests have indicated that both carbon oxysulfide and carbon disulfide are completely removed from gases by scrubbing in the manner described with the piperidine-ethanol solution. Hydrogen sulfide is also removed as dipiperidine hydrosulfide, but this material is transparent when it is present in low to moderate concentrations. Mercaptans and other sulfur compounds such as dimethyl sulfide do not effect this determination; either they do not react with the piperidine or the reaction products are relatively transparent.

In Table III the analytical results for a number of synthetic samples are given. The synthetic gas samples were prepared by successive dilutions of gas samples using a precision manometer to measure all gas pressures. Because the errors involved in preparing the samples in this manner are large, it is apparent that the values given in Table III are only indicative of the results that can be obtained. It is believed that the information contained in Tables I and II, inclusive, in addition to the fact that carbon disulfide and carbon oxysulfide are completely removed from the gas by the piperidine-ethanol solution, is more pertinent in evaluating this procedure than are the results shown in Table III.

Table III. Determination of Thiophene, Carbon Oxysulfide, and Carbon Disulfide in Synthetic Producer Gas

Concentration of Thiophene		Concentration of Carbon Oxysulfide		Concentration of Carbon Disulfide		Concentration of Benzene
Present	Found	Present	Found	Present	Found	Present
Mg. per liter of gas						
15	13	0	0	0	0	0
15	18	15	13	25	28	50
15	16	0	0	25	23	50
15	14	15	17	0	2	50

The speed of analysis and the very low organic sulfur concentrations that can be determined are the distinguishing characteristics of this method. The simplicity of the techniques involved makes it particularly valuable as a control procedure.

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Gas Analysis Apparatus Employing the Velocity of Sound

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The composition of certain binary gas mixtures can be determined by measuring the velocity of sound in the gas. An audio-frequency oscillator (1000 to 3000 cycles per second) is used to generate a stable, sine wave signal which operates a small dynamic speaker placed at one end of a brass tube through which the gas sample flows. A sensitive microphone at the opposite end of the tube gives a maximum or minimum signal, depending upon the resonance conditions of the tube, which depend on the length of the tube and the values of the density and the specific heats of the components of the mixture. For a given tube length and sound frequency, the intensity of the microphone signal is a trigonometric function of the composition of the mixture. The microphone signal is amplified electronically and registered on a meter that can be calibrated in terms of the composition of the gas mixture and gives a continuous reading of the composition of gas flowing through the tube. The device has been applied to analysis of mixtures of hydrogen in air, full scale representing 10% hydrogen, in any range between 0 and 100%. The electronic circuit provides an electrical signal when one component of the mixture exceeds a preset value. The apparatus has been used for analysis of methane-air and carbon dioxide–air mixtures.

IN 1895, in a paper hardly longer than this paragraph, Hardy described a method for the determination of illuminating gas in air, making use of the velocity of sound in the gas mixture (*5*). Sound of frequency of about 500 vibrations per second was passed through two tubes, one containing air and the other the gas mixture, and into a resonating box covered with a diaphragm. The number of beats produced in the resonator in a 20-second interval, recorded electromechanically, gave a fairly sensitive measure of low concentrations of illuminating gas in air.

Somewhat later, acoustical methods were used by Haber (*4*) for the analysis of methane-air mixtures and by Hurwitz (*6*) for the determination of air in hydrogen. Dual organ pipes containing the mixture and a reference gas were used by both workers; the beats produced were counted or the length of one pipe was varied until no beats were heard.

A later apparatus by Griffiths (*2*) of the National Physical Laboratory employed a quartz crystal–controlled electronic oscillator as the sound source; a face of the quartz crystal was placed directly in the gas chamber to generate the sound. A movable reflector on a micrometer screw was adjusted to nodal points, as indicated by a sharp rise in the plate current of the oscillating vacuum tube. A plot of the distance between nodes against the percentage of carbon dioxide in air was almost linear. At the frequency used by Griffiths, 40,000 cycles per second, the variation in the internodal distance on passing from pure air to pure carbon dioxide was about 1 mm., so that the accuracy was limited by the precision of two readings of the position of the reflector, corresponding to 1 to 2% of carbon dioxide.

A few other studies, although not directly concerned with the analysis of gas mixtures, have a bearing on the problem. The work of Dixon and Greenwood (*1*), in which the velocity of sound was measured using a double Kundt tube and powder patterns to determine nodal distances, was directed to the determination of the value of γ of gas mixtures—that is, the ratio of the specific heats at constant pressure and constant volume. The investigations of Sherratt and Awbery (*15*) and Kaye and Sherratt (*7*) involved a comprehensive study of the velocity of sound in tubes. The sound was generated by a crystal-controlled oscillator and an electronic pickup device was employed to determine the nodal positions.

As analytical methods, these earlier devices leave something to be desired, with respect to both accuracy and convenience. All require close observation and subsequent calculation by the operator, and although the low relative accuracy of the three apparatus based on the counting of beats is satisfactory for determining approximately the small amounts of impurities in air, the accuracy of the Griffiths apparatus, which covered the entire concentration range from pure air to pure carbon dioxide, was considerably less than that of the commonly used gas-volumetric equipment.

The instrument described in this paper, which is an electronic device based on the velocity of sound in the gas mixture, furnishes a continuous reading of the composition of the gas passing through it and also operates auxiliary equipment through a relay that may be set to close at any desired gas composition. Like any physical method of analysis, its applications are limited to binary systems or their equivalent. Variation in a number of the components of the apparatus permits a considerable variation in the range of gas composition covered and the general order of accuracy is considerably better at the higher sensitivity settings than that of the unmodified conventional gas-volumetric equipment. Audio-frequency sound is generated by an electronic oscillator which has been made sufficiently stable without resort to crystal control. The sound is delivered by means of a speaker to a tube through which the sample passes, and the sound at the far end of the tube is picked up by a small microphone. The distance between the speaker and microphone can be varied by a screw. The output of the microphone is amplified by a two-stage audio-amplifier and measured by a diode detector, giving indication on a microvoltmeter on the panel of the instrument. The relay circuit operates in parallel with the diode detector. The range and accuracy of the instrument depend on the nature of the gases composing the mixture and the frequency of sound used. The apparatus has been used for the analysis of hydrogen-air, carbon dioxide-air, and methane-air mixtures, but its utility is not confined to these combinations of gases. An apparatus working on the same principle has been constructed by the General Electric Company (*11, 12*), but this differs from the apparatus here described, depending on frequency variation rather than on a fixed frequency, fixed tube-length, variable pickup method.

Table I. Properties of a Few Common Gases Related to Velocity of Sound in Gases

Gas	Density at 0°, G. per Cc., $d \times 10^3$	$\gamma = \dfrac{C_p}{C_v}$	$\sqrt{\dfrac{\gamma}{d}}$	Wave Length, λ, Cm. for $f = 2650$ C.P.S.
Air	1.2929	1.40	32.90	12.62
Hydrogen	0.08988	1.41	125.2	48.02
Carbon dioxide	1.9769	1.30	25.64	9.832
Methane	0.7168	1.31	42.75	16.39
Carbon monoxide	1.2504	1.40	33.46	12.83
Ethylene	1.2604	1.25	31.49	12.07
Oxygen	1.4290	1.40	31.30	12.00

THEORETICAL ASPECTS

The velocity of sound in an unconfined gas is given by the expression

$$v = \sqrt{\frac{\gamma p}{d}} \qquad (1)$$

where v is the velocity in centimeters per second, γ the ratio of the specific heats at constant pressure and constant volume, p the pressure in dynes per square centimeter, and d the density in grams per cubic centimeter. It is assumed that this expression applies equally to a gas confined in a smooth-walled tube, a fair approximation if the tube diameter is not too small, 20 mm. or greater. Combining the well-known relation of velocity, wave length, and frequency

$$v = \lambda f \qquad (2)$$

with Equation 1 yields

$$\lambda = \frac{1}{f} \sqrt{\frac{\gamma p}{d}} \qquad (3)$$

for the wave length in centimeters, the frequency being in cycles per second.

It is apparent that for a given frequency and pressure the wave length will depend on two properties of the gas, the ratio of the specific heats and the density, and that a method of analysis based on measurement of the velocity of sound will be most applicable to mixtures of gases, the components of which have significant differences in the ratio of γ to d. Values of γ and d for a few common gases are given in Table I, together with the wave length computed for the particular frequency used in the apparatus being described.

The ideal gas law may be combined with Equation 1, yielding

$$v = \sqrt{\frac{\gamma p}{\dfrac{pM}{RT}}} \qquad (4)$$

in which the term p cancels. The velocity of sound in the gas thus is independent of the pressure as far as the gas law holds. In an analytical apparatus based on the velocity of sound, therefore, no great attention need be paid to the pressure, and the low pressure differences necessary to force the gas through the sound tube will have no effect on the results.

Because of its low density, the method should be well suited to the determination of hydrogen in a mixture with air or with any of the common gases. It should work well also for carbon dioxide in air but should be less sensitive for methane in air, still less for oxygen or ethylene in air, and practically inapplicable to carbon monoxide-air mixtures. This was found to be the case.

In the apparatus described, actual measurement of the wave length is not made. The length of the sound tube can be varied by means of a screw, but this is only for convenience in establishing

a zero setting. Rather, a sound tube of fixed length is used and the amplitude of the sound wave at the microphone is measured. The amplitude varies as shown in Figure 1 and is measured by a microphone, located at section BB', coupled to a vacuum tube voltmeter. The speaker is located at CC'.
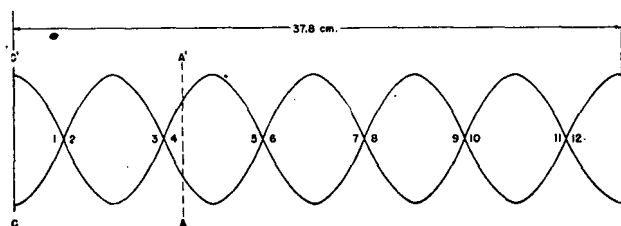
Figure 1. Number of Quarter Wave Lengths Present with Air in Sound Tube

Speaker at CC', microphone at BB'

If the approximate frequency is known, a moderately accurate measure of the distance between the speaker and microphone makes possible a calculation of the number of quarter wave lengths in the tube when it contains air or some other pure gas by using the value of γ as calculated in Table I.

For example, with air in the sound tube and a distance from the speaker to the microphone of 37.8 cm., the microphone was at a point of maximum amplitude 12 quarter wave lengths from the speaker. For pure hydrogen in the sound tube, there are only 3.15 quarter wave lengths in the tube—that is, section AA' is then located at BB'. As the composition of the gas in the sound tube is varied from pure air to pure hydrogen, there is a succession of changes in amplitude at BB'. These are recorded by the vacuum tube voltmeter; the meter passes from a maximum to a minimum and back for each half wave length. As air is replaced by hydrogen, it goes through five maxima (counting the original) and four minima. The vacuum tube voltmeter can be adjusted to give a full scale change for a movement of one quarter wave length past the microphone. Thus, the meter scale will be covered eight times in going from 0 to 100% hydrogen and the full scale of the meter will thus correspond to about 100 to 8 or 12.5% of hydrogen. Further adjustments in the amplifier and the vacuum tube voltmeter make it possible to double this sensitivity—at full sensitivity of the amplifier and vacuum tube voltmeter the full scale will correspond to a change of 6% in the hydrogen concentration. The apparatus is so designed that this 6% range may be taken at any concentration range from 0 to 100% hydrogen.

In the case of carbon dioxide, the wave length is shortened as it replaces air in the sound tube. With pure carbon dioxide in the tube, there are 15.2 quarter wave lengths between the speaker and the microphone. On passing from pure air to pure carbon dioxide the vacuum tube voltmeter goes through two maxima and two minima, counting as before. Thus, full scale deflection represents 100 to 3 or 33.3% carbon dioxide. If the maximum sensitivity of the amplifier and vacuum tube voltmeter is used, a full scale deflection can be made to cover 16% carbon dioxide.

With methane in the sound tube and the same length of tube as before, 37.8 cm., 9.2 quarter wave lengths are present. As air in the sound tube is replaced gradually by methane, the meter moves from the original maximum position to a minimum and then slightly past the next maximum. Thus, full scale represents about 40% methane and, at maximum sensitivity of the voltmeter, full scale corresponds to about 20% methane.

In the case of pure ethylene, 12.5 quarter wave lengths are present and with pure oxygen, 12.6. On passing from air to pure ethylene or pure oxygen the vacuum tube voltmeter does not reach the first minimum value. For ethylene a deflection of 30 divisions (50-division meter) was obtained and in the case of oxygen a change of 32 divisions. At the maximum amplification of the vacuum tube voltmeter, a deflection of one division is obtained for about 1% of ethylene or oxygen admixed with air. In the case of carbon monoxide, 11.8 quarter wave lengths are present in the tube, and the change on going from pure air to pure carbon monoxide is negligible.
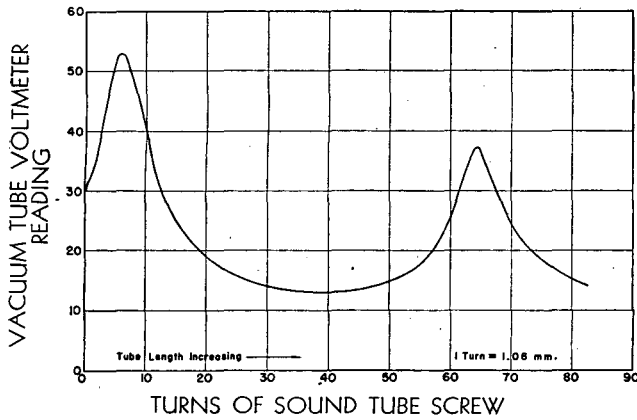
Figure 2. Effect of Changing Length of Sound Tube

1 revolution equal to 1.06 mm.

As a means of judging the maximum accuracy to be expected for a given mixture, the number of quarter wave lengths passing over the face of the pickup should be calculated. This number divided into 100 gives the percentage of gas for a full scale de-

flection. The maximum sensitivity can be made twice this by increasing the amplification of the vacuum tube voltmeter.

The sound at the maximum points decreases on passing down the sound tube away from the speaker. Thus, with a stream of dry air passing slowly through the tube, the data of Figure 2 were obtained on changing the length of the sound tube through two successive maxima. As the pitch of the screw was known, the number of revolutions of the screw gave the distance between nodes from which the frequency of the oscillator was calculated, using 33,200 cm. per second as the velocity of sound. The decrease in the intensity is due to a damping factor, characteristic of the tube and also dependent on the viscosity, heat conduction, and density of the gas in the tube. The tube walls should be fairly smooth to keep the damping factor as low as possible.

APPARATUS

The electrical circuit of the apparatus, shown in Figure 3, was divided into four parts: the oscillator, the amplifier, the detector, and the relay. Of these, the oscillator circuit was the most critical because the frequency and amplitude of the signal delivered to the sound tube must be constant if a satisfactory calibration is to be secured and maintained.

The oscillator employed was a doubly stabilized, tuned grid oscillator. C_1 and C_2 were plate- and grid-stabilizing con-
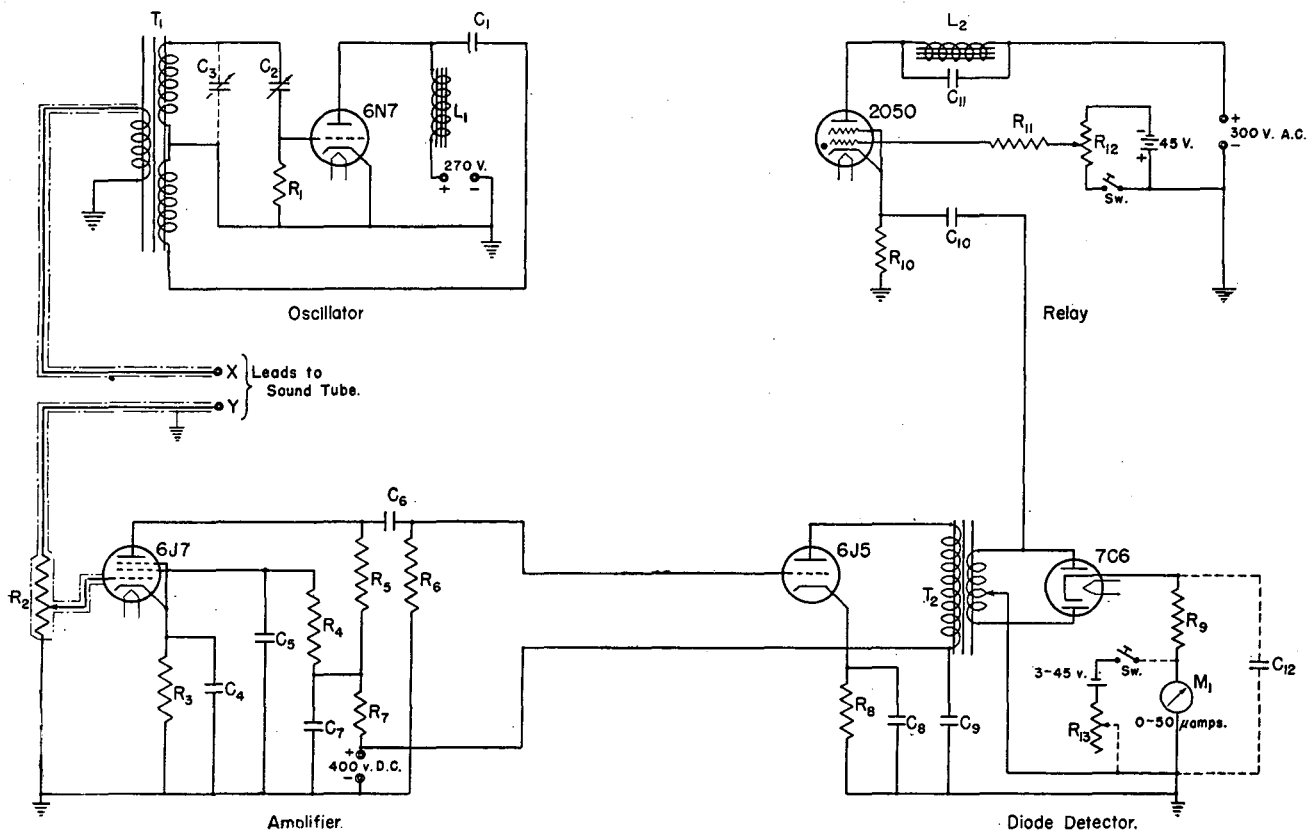
Figure 3. Electrical Circuit

R_1. 300 ohms, 10 watts
R_2, R_6, R_9. 1 megohm, 1 watt
R_3. 2200 ohms, 2 watts
R_4. 2.9 megohm, 1 watt
R_5. 0.5 megohm, 1 watt
R_7. 0.1 megohm, 1 watt
R_8. 1200 ohms, 2 watts
R_{10}. 10,000 ohms, 10 watts
R_{11}. 0.56 megohm, 1 watt
R_{12}. 2 megohms, 1 watt
R_{13}. 1 megohm, 2 watt
L_1. 30 mh., 110 mamp.
L_2. 10,000-ohm relay coil
T_1. 19-ohm primary, center tapped, B. and S. No. 18 wire; 15 turns for output coil

T_2. Thordarson T-19D06
M_1. Weston, model 801, 0–50 μamp. range
C_1. 0.03 μf.
C_2. 0.001 μf., 450 $\mu\mu$f., adjustable condenser and 0.01–0.001 μ. decade in ten steps, all in parallel
C_3. Absent in 2000–3000 cycles per second range, 0.01–0.10 μf. n ten steps for 500–2000 cycles.
C_4, C_7, C_8, C_9. 4–8 μf. electrolytics
C_{11}. 4 μf.
C_5. 0.04 μf.
C_6. 0.003 μf.
C_{12}, C_{10}. 0.1 μf.

densers; C_1 also served as a blocking condenser for the direct current supply, while C_2 had the additional function of furnishing grid bias. C_3 was removed entirely for frequencies above 1500 cycles per second and was used for tuning at lower frequencies. C_2 was used for tuning at frequencies from 1500 to 3000 cycles per second. For maximum stabilization, C_2 and C_1 must both be changed if a wide range of tuning is desired. The circuit values are given for good stabilization and tuning in the range of 2000 to 3000 cycles per second. R_1, which is fairly critical, must be increased for lower frequencies. If R_1 is too high, the sine wave output is first distorted and at higher values motor boating begins.

It is important that the power supplies furnish constant voltage. A Sola constant-voltage transformer was used to stabilize the line voltage. The oscillator required about 80 milliamperes at 270 volts for its operation. The total grid current was about 5 milliamperes. Thus, the 6N7 triode was operating far below its rated capacity. The stability of the oscillator was greatly increased by cooling the 6N7 tube with water. A glass jacket was placed on the tube with rubber stoppers cut to about 1.2-cm. thickness and water inlet and outlets brought through the rubber. T_1 was wound with No. 18 B. and S. copper wire, cotton covered and lacquered. The output coil and the larger, center-tapped coil were placed on a straight core of transformer laminations 2.5 × 2.5 × 22 cm. in size. The output coil consisted of about fifteen turns; its resistance was very low. The resistance of the larger coil was 9.5 ohms on either side of the center tap.

More stable audio-oscillators have been described (3, 10, 13, 14) but they are more complex than the one described here. It was the aim to keep the circuit as simple as possible and yet obtain accuracy comparable to the conventional, gas-volumetric methods.

The output of the oscillator was coupled to the coil of a dynamic speaker 6.2 cm. in diameter, placed at one end of the sound tube. The details of the sound tube are shown in Figure 4. It was constructed of brass tubing of 2.5-mm. wall thickness and 4 cm. in outside diameter. The length of the tube was adjustable over a range of 10 cm., the maximum length being 44 cm., by means of a screw which moved the speaker and an attached, telescoping section of the sound tube. One revolution of the screw moved the speaker 1.06 mm. The gas inlet was placed directly in front of the microphone element and the outlet directly in front of the speaker. Both inlet and outlet were made of 6-mm. copper tubing. When small tubing was used, the inlet and outlet caused no interference with the wave pattern in the sound tube. A slight gas leakage was allowed behind both the speaker and the microphone to prevent gas being trapped in these cavities.

Because one side of the speaker and one side of the microphone were grounded, it was necessary to run only two leads to the sound tube. A two-conductor, shielded cable was used. The sound tube was connected to the main instrument case for the common ground through the cable shielding. A
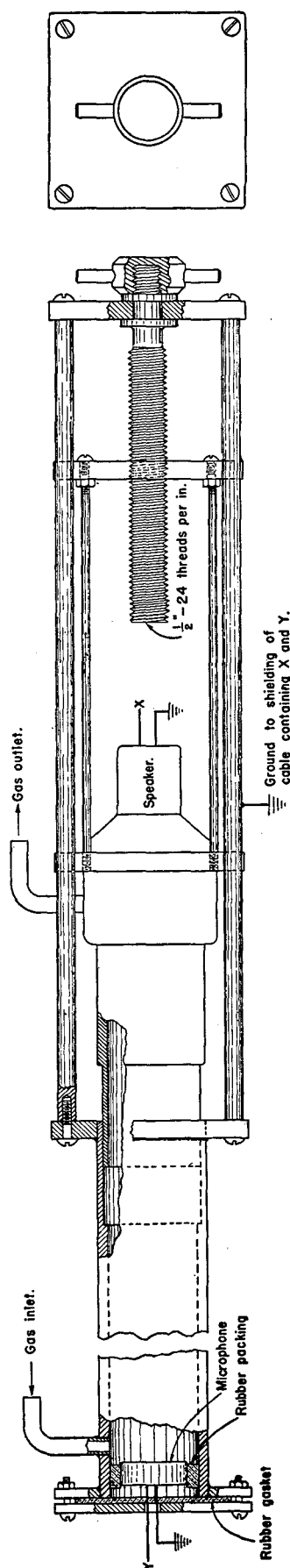

Figure 4. Sound Tube

conventional, two-stage, resistance-coupled amplifier and a push-pull diode detector were used to amplify and register the signal picked up by the microphone. A battery was used to balance out high currents through the vacuum tube voltmeter. Thus, the signal could be at a maximum and the meter current limited to 50 microamperes. With this arrangement it was possible to obtain full-scale deflections when only one eighth or one tenth of a wave length moved past the microphone.

The relay circuit employed a grid-controlled thyratron. An alternating current plate supply was used so that the direct current battery bias could cut off the tube. The unconventional method of applying the signal to the grid-controlled thyratron was used only because it caused no reaction in the diode detector when the thyratron fired. When the cathode was grounded and the alternating current signal superimposed on the direct current bias, a great deal of interaction occurred.

The relay circuit was arranged so that the relay could be adjusted to close at any point on the vacuum tube voltmeter scale by adjusting R_{12}. The thyratron fired as the current in the vacuum tube voltmeter increased to the reading desired and was biased out as the current dropped past the same scale reading. The closing of the relay could be set within ±1 scale division. If the biasing battery failed, the tube fired continuously regardless of the reading of the vacuum tube voltmeter and the position of the switch. If the vacuum tube voltmeter swung too fast, the relay did not trip at the preset value because of a 3-second time delay which is governed by the value of C_{11}. Decreasing C_{11} decreased this time delay but also tended to make the relay chatter.

CALIBRATION

After the instrument was turned on, a period of 1 hour was allowed before beginning a calibration. With dry air flowing through the sound tube, the microphone was first set on a point of maximum amplitude, by either tuning the frequency of the oscillator or changing the length of the sound tube. The frequency was changed by varying the 3-gang, 450 micro-microfarad air condenser in the oscillator circuit. The length of the sound tube was varied by means of a screw moving the speaker and the attached telescoping part of the sound tube. The points of maximum amplitude were a great deal sharper than the minimum points (Figure 2). The vacuum tube voltmeter was then set at the full scale reading, 50.0, by adjusting the signal input by varying R_1.

The instrument was calibrated with mixtures of hydrogen and air, carbon dioxide and air, and methane and air. With the instrument properly zeroed, the dried gas mixture was passed through the sound tube. A steady reading was obtained rapidly after approximately 2.5 liters of gas had passed through the tube. Samples of gas were taken for analysis at the outlet of the sound chamber; readings of the vacuum tube voltmeter were checked before and after the sample was collected, to make certain there was no change. Care was taken in collecting the samples, so that at no time was the pressure in the sound tube reduced below that of the atmosphere. The gas was forced

through the drying tube and the sound tube under a hydrostatic head of 1 meter of water. Changes of this head of ±25 cm. had no effect on the reading of the instrument.

Calibration curves are shown in Figure 5 for hydrogen-air mixtures that were analyzed by passage over platinized silica gel (8). Samples of 200 ml. were analyzed to increase the accuracy of the lower percentage mixtures.

In Figure 5 are shown four calibration curves for hydrogen-air mixtures.

The effect of increasing the frequency can be seen by comparing curves 1 and 3. In the circuit diagram, Figure 3, the diode detector circuit is shown with a condenser, C_{12}, and a balancing voltage and series resistor, R_{13}, in dashed lines. These two branches were not present in the circuit when curves 1 and 3 were determined, and the meter reading was proportional to the r.m.s. voltage. The condenser, C_{12}, when placed in the circuit, changed the meter reading, making it proportional to the peak voltage. The effect of adding C_{12} can be seen by comparing curves 2 and 3. Finally the balancing voltage and series resistor, R_{13}, were added. The maximum signal was used by increasing R_2, and the excess current through the meter was balanced out so as to bring the meter reading to full scale as before, with dry air in the sound tube. The effect of this can be seen by comparing curves 2 and 4 where peak voltages were followed at the same frequency. Twelve volts were used for balancing voltage in determining curve 4, and the resistance, R_{13}, was low enough to cause an
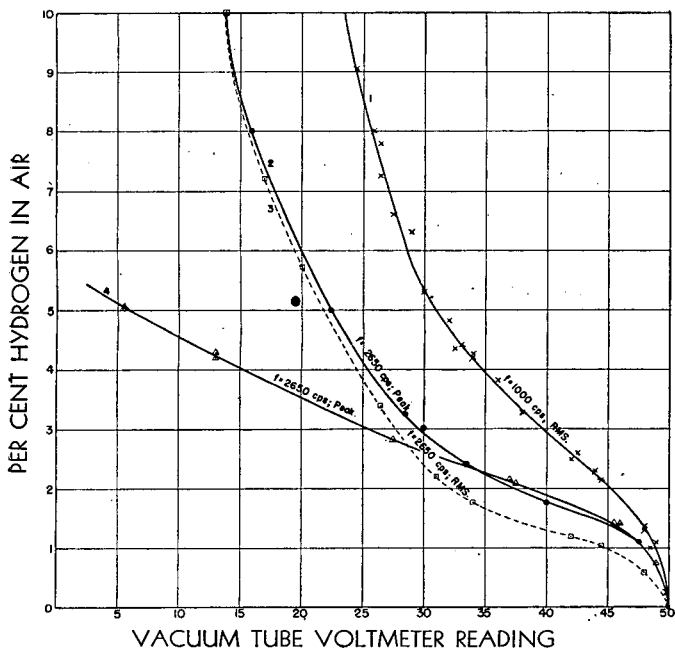

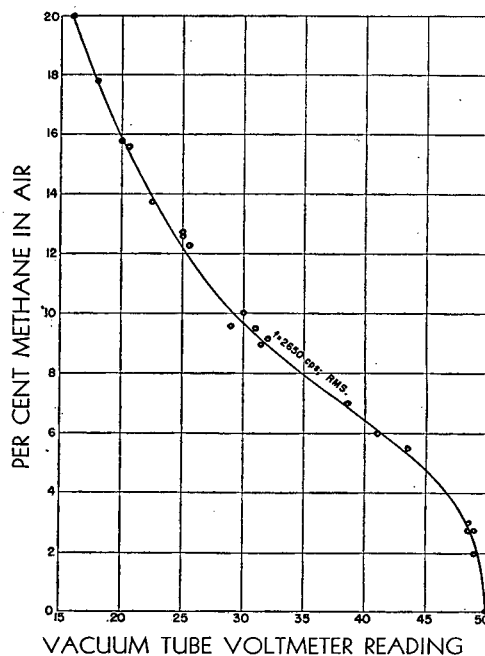**Figure 5. Calibration Curves for Hydrogen-Air Mixtures**
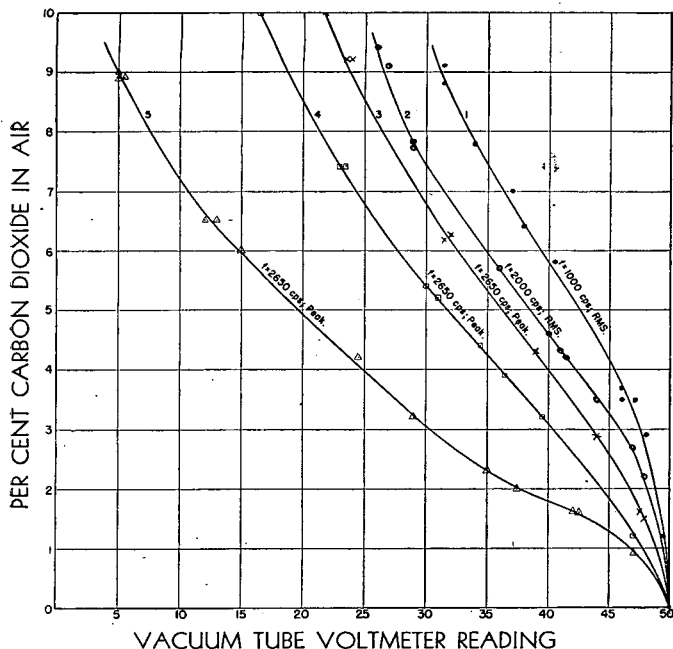

Figure 7. Calibration Curve for Methane-Air Mixtures

appreciable loss in sensitivity, as is shown by the elevation of curve 4 above 2 at low percentages of hydrogen. When the increased sensitivity is needed, the balancing voltage must be increased so that the value of R_{13} becomes large compared to the meter resistance.

Calibration curves are shown in Figure 6, for carbon dioxide-air mixtures which were analyzed by absorbing the carbon dioxide in 30% potassium hydroxide. Samples of 200 ml. were analyzed at the lower percentages of carbon dioxide.

The effect of increasing the frequency is shown by curves 1 and 2 where r.m.s. voltages were measured by the detector and no balancing voltage was used. In curves 3, 4, and 5, the peak voltages were measured and balancing voltages were used. In curve 3, 12 volts were used for the balancing voltage, and in curve 4, 45 volts were used. The latter curve shows a marked increase in sensitivity, as R_{13} was increased to approximately 1 megohm and thus a negligible amount of current by-passed the meter through the balancing branch. Curve 5 was determined, using a longer sound tube, and a distance of 85 cm. between the speaker and microphone. When a sound pattern was used as shown in Figure 1, there were 27 quarter wave lengths in the 85-cm. tube containing dry air and 34.6 quarter wave lengths in the same tube containing dry carbon dioxide. Thus the meter passed through four maximum and four minimum deflections as the air was slowly replaced by carbon dioxide. In the 37.8-cm. tube, the

Figure 6. Calibration Curves for Carbon Dioxide-Air Mixtures

meter deflections showed only two maxima and two minima. Thus the sensitivity can be increased by lengthening the sound tube. All the calibration curves were determined on a 37.8-cm. tube except curve 5 in Figure 6. An 85-cm. tube was used for curve 5; all other settings remained the same as formerly used in determining curve 4 in Figure 6. The increased sensitivity was accompanied by an increase in the random fluctuations of the vacuum tube voltmeter, due to slight variations of the oscillator. The meter fluctuated about one to two divisions in an hour, but remained steady within a scale division long enough to run a gas mixture through the tube after calibration.

When the frequency was increased above 3000 cycles per second, the nodal points were not so sharp, probably because of transverse waves. A decrease in the tube diameter would allow a further increase in the frequency. However, increased frequency would necessitate a greater stability in the oscillator. Thus in the present work, curve 5 represents the practical limit of sensitivity that can be obtained with the oscillator used. The key to greater sensitivity lies in a more stable oscillator. The sensitivity can then be achieved by increasing the tube length, increasing the amplification of the signal from the microphone, and increasing the frequency within the limits of complication of the sound pattern by transverse waves.

At frequencies below 1500 cycles per second methane-air mixtures did not give a sufficiently large change to yield satisfactory accuracy. However, satisfactory results were obtained at a frequency of 2650 cycles per second, as shown in Figure 7. The methane-air mixtures were analyzed by the method of Kobe and Barnet (9) using platinized silica gel. The curve shown in Figure 7 was determined without the balancing voltage and measuring

the r.m.s. voltage. The instrument settings were identical to those of curve 3 in Figure 5.

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Determination of Refractive Index of Polymers

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A review has shown that the Abbe refractometer has been used most extensively for the determination of refractive indexes of both opaque and transparent polymers. The determination requires the use of a specimen with polished surfaces or a film of the polymer, solvent, or melt cast on the prism of the instrument or on a glass form. Transmitted or totally reflected light or the grazing incidence technique is used. Immersion methods have also been developed. Other methods for determining the refractive index of polymers have been used. This discussion summarizes and correlates the salient features of the various procedures and the preferred techniques used for specific polymer types.

REFRACTIVE index data for polymers are of interest in several ways. The value is characteristic and can be used for identification purposes (9). With density data, molecular or unit refractivities can be observed and the values thus obtained agree with values calculated for the polymer unit (13, 14, 41, 44). The knowledge of refractive index is necessary in optical applications of transparent polymers. The refractive index–temperature data show the second-order phase transition and can be used to locate the transition temperature (8, 42). These and other (2, 10, 24, 26, 28) uses for refractive index data of polymers suggested the advisability of compiling the available information on the methods of determination of the index and this study was therefore undertaken.

Most polymers are amorphous and are, therefore, isotropic. Their refractive indexes are the same for any direction which the path of light may take through the solid. Methods for determining the refractive indexes of amorphous polymers have been described carefully in the literature and this discussion is con-

cerned primarily with these methods. A few polymers are, however, markedly crystalline and are birefringent. Polyethylene, polyvinylidene chloride, polyamides, cellulose and some of its derivatives, and polytetrafluoroethylene are crystalline under ordinary conditions. Rubber is crystalline under some conditions (30, 31). Polyethylene has been observed to be birefringent and the values of the two indexes as a function of temperature have been reported (7, 12). The technique used in the determination of the birefringence of polyethylene was not detailed. Rubber is birefringent when cooled or stretched and an immersion technique for determining the values of the two refractive indexes has been carefully described (30, 31).

In determining the refractive index of amorphous polymers use is usually made of critical angle instruments, immersion techniques, and measurement of apparent thickness. Spectrometers (11, 15), interferometers (20, 37), or specially designed refractometers (1, 5, 11, 15, 20, 25) have not been extensively used. The use of an interferometer to measure the change in density of

rubber with change in temperature has been reported (*45*). A spectrometric method using rubber prisms has been described (*44*) and Jelley (*16*) has successfully used the Leitz-Jelley micro-refractometer by evaporating a toluene solution of polystyrene in the bevel of the instrument. Both the spectrometer and interferometer have been used to determine the refractive index of solids with a high degree of accuracy and can conceivably be adapted to determination of the refractive index of polymers. Such high precision methods are of limited usefulness with polymers because extreme purity of sample is often difficult to obtain.

METHODS USING CRITICAL ANGLE INSTRUMENTS

The Abbe refractometer is a critical angle instrument. The theory for the construction of such an instrument is presented in various discussions (*5, 6, 27, 36, 37, 38*). The constructional factors determining the accuracy of critical angle instruments (*34*) and errors introduced in use of the Abbe refractometer (*35*) have been discussed.

The improved Abbe refractometer may be used in one of three ways, classified by the light paths (*40*).

(1) The method of total reflection is used for opaque solids and liquids. The shield covering the front side of the refracting (upper or fixed) prism is swung open. Light passes through the refracting prism, is refracted and reflected by the specimen, and passes back through the refracting prism to the view telescope. (2) The method of transmission is used for liquids or thin sheets of transparent polymers. Light is reflected by the mirror through the illuminating (lower or movable) prism, and passes through the specimen, where it is refracted into the refracting prism and into the view telescope. (3) The method of grazing incidence is used for transparent solids of appreciable thickness. The illuminating prism is swung aside and the light is refracted by the specimen into the refracting prism and passes on to the view telescope. The first method does not give so strong a contrast as the latter two.

Transparent polymers are examined by means of the transmitted light or light at grazing incidence. In either case the principal problem in determining the refractive index of the polymer is in mounting the specimen. Several methods have been devised. The A.S.T.M. method (*3*) employs a specimen about $1 \times 2 \times 0.5$ cm. with the 1×2 cm. surface polished flat and one end surface polished perpendicular to the first. The edge of intersection must not be beveled. The large, flat surface is attached to the refracting prism with a contacting liquid inert to the specimen and of higher refractive index than the specimen. The illumination is then by grazing incidence. The remainder of the observation is made according to the usual procedures with liquids. Temperature control is maintained and dispersion noted.

For many polymers, suitable inert contact liquids are not available. The A.S.T.M. directions suggest the use of α-bromonaphthalene or other organic liquids. These often attack the polymers, as can be seen in a changing value for the refractive index during the first few minutes. In such cases the use of potassium mercuric iodide is suggested but it should be used carefully because experience has shown that this liquid readily attacks the glass prisms (*16*). The use of cadmium borotungstate, n_D^{20} 1.636 for a saturated solution, has been found not to attack the glass within reasonable contact time and is less poisonous (*16*). Values reproducible to ± 3 in the fifth place have been obtained by using polished moldings of polystyrene, poly-α-methylstyrene, and poly-p-chlorostyrene (*32*). A Bausch & Lomb horizontal Abbe refractometer was used with a potassium iodide–mercuric iodide solution containing a little glycerol as contact liquid.

Various methods have been devised for mounting the specimen to be viewed by transmitted light.

West (*40*) suggests pouring molten material onto the prism, with or without closing the back prism, and making readings after solidification. Use of the prism in this manner ties up the instrument and may damage the prism. To obviate these drawbacks the polymer is mounted on a glass flat having a refractive index higher than the polymer under test. Microscope slide glass is satisfactory for materials of refractive index below 1.51, and flint glass with a value of 1.63 is also used. The uncoated side of the flat is then held to the upper prism with a contact liquid. Instead of melting the specimen, a technique not often useful with polymers, the polymer may be dissolved in a volatile solvent and evaporated on the forms or on the prism (*41*). However, traces of solvent in a solvent cast film can materially alter the refractive index, especially below the second-order transition temperature (*43*). Care must be taken to avoid scratching the prisms if films are cast directly on them. Illumination of transparent samples by polarized light using the total reflection technique (*35*) has been reported to give very good results (*16*).

Perhaps the most direct method of mounting a specimen for the determination was used by McPherson (*18, 19, 21*). A thin film of the polymer is clamped securely between the prisms and the observation made with transmitted light as with liquids. By warming the prisms intimate contact is obtained and sharp fields result. This method is useful with soft materials such as well milled rubber but must be used with caution because the stresses put on the prisms by tight clamping may displace or loosen the prisms and thereby impair the accuracy of the instrument or measurement and because the finite thickness of the film introduces an error into the measurement. Compressing a thick film sufficiently to alter its density will also introduce an error in the measurement. Extreme caution must be exercised to avoid scratching the very soft glass of the prism (*16*) and to avoid loosening the prism cement by excessive heating.

More or less opaque substances are studied by the total reflection method (*22*). The contrast is not so great as in the transmission or the grazing incidence methods, especially when the more opaque specimens are being tested. According to West (*40*), with thin films the film-air boundary gives reflections that may weaken the contrast. The bright part of the field is due to totally reflected light—light that enters the specimen at the critical angle or greater. The darker portion of the field is due to ordinarily reflected light; part of the light passes through the specimen and is lost as far as the field is concerned. The contrast is sufficient for thick specimens, but not for thin films. West presents three methods for increasing contrast.

(1) The area of illumination and the angle at which the light strikes the refracting prism are varied. (2) The internal reflection at the film-air boundary is suppressed by increasing the film thickness or by adding a drop of inert liquid of higher refractive index than the film and closing the illuminating prism, thus reducing stray light. Stray light increases the weak part of the field, decreasing contrast. This method is not always possible or convenient. (3) Polarized light is used to illuminate the sample.

The Pulfrich refractometer has been used to determine the refractive index of rubber (*21*). Reports describing the use of other critical angle instruments with polymers have not been found.

IMMERSION METHODS

Refractive index can be determined by immersion methods (*7, 9, 13, 17, 25, 27, 29, 30, 31, 33*), which are particularly useful when only small samples of the polymer are available or when the material is to be conserved. The refractive index of the sample is matched with that of an inert liquid. The sample is immersed in a series of inert liquids of varying refractive index and observed microscopically. The two principal methods of comparing the refractive index of the sample with that of the liquid in which it is immersed are the Becke line method and the oblique illumination method; the former is the more accurate of the two (*29*). In order to reduce the number of liquid standards necessary for a given sample several methods have been devised (*17*). Among these may be mentioned: changing the temperature of the immersion liquid, varying the wave length of the light used for observation, and mixing two liquids of different refractive indexes and measuring the refractive index of the mixed liquids after a match has been obtained.

Table I. Methods of Determining Refractive Index

Polymer	Method Used[a]	Reference	Accuracy[b]
Condensation types			
Phenol-formaldehyde	Immersion	9	Third
	Liquid[c]	26	....
Urea-formaldehyde	Immersion	9	Third
Glyptals	Immersion	9	Third
Polyamides	Immersion	7	Third
	Film P	43	Third
Silicone (low mol. wt.)	Liquid[c]	39	Fourth
Natural types			
Proteins	In solution	4	Fourth
Cellulose	Immersion	13	Fourth
Cellulose ethers	Film S, P	43	Fourth
Rubber	Immersion	30, 31	Third
	Spectrometric	44	Fourth
	Film S, P	18, 19, 21	Fourth
	Reflection	22	Fourth
Addition types			
Polyethylene	Immersion	7	Third
	Film P	43	Third
Butadiene copolymers	Film S, P	43	Fourth
Polystyrene	Solution cast	16	Fourth
	Polished block	32	Fifth
Poly-α-methylstyrene	Polished block	32	Fifth
Poly-p-chlorostyrene	Polished block	32	Fifth
Polyisobutylene	Film P	43	Fourth
Polyvinyl acetate and chloroacetate	Film S, P	36, 42	Fourth
Polyvinyl chloride-acetate	Film P	43	Fourth
Polytetrafluoroethylene	Immersion	7	Third
	Film P	43	Third (?)
Neoprene	Film P	43	Third
Polyethyl acrylate	Film P	43	Fourth
Styrene-maleic anhydride copolymer	Polished block	36	Fourth

[a] S, solvent cast. P, pressed.

[b] Results reported to third place or fourth place as indicated. Accuracy usually refers to sharpness with which reading can be made; not to deviation among samples except for rubber (21, 22), polyvinyl acetate (42), and polystyrene (32).

[c] Polymer examined as liquid.

Hermans et al. (13) have used an immersion method in determining the refractive indexes of viscose fibers. The fiber is immersed in a mixture of butyl stearate and tricresyl phosphate of suitable refractive index and observed with a polarizing microscope according to the Becke method. The determination of the two refractive indexes of birefringent rubber has been mentioned (30, 31). Billmeyer (7) has recently described an immersion method for polyethylene, nylon, and polytetrafluoroethylene.

Disadvantages of the immersion methods include the necessity of having liquid standards available which are inert towards the polymers being tested and whose refractive index does not change on exposure to air over an appreciable period of time. Control of temperature is difficult unless special heating devices are affixed to the microscope stage. The degree of accuracy obtained is usually not so great as that obtained by the use of critical angle instruments.

MEASUREMENT OF APPARENT THICKNESS

A method of determining the apparent thickness is described by the American Society for Testing Materials (3).

A microscope with a magnifying power of at least 200 diameters is used. The specimen, 0.25 inch thick with two parallel surfaces, is placed with the better polished surface nearer the objective. The microscope is focused through the specimen on the bottom surface and the longitudinal displacement of the lens tube is recorded. Without moving the specimen, the microscope is refocused on the top of the specimen and this displacement of the lens tube is recorded. Both displacements are read to within 0.001 inch. The difference in the readings is the apparent thickness of the specimen. The index of refraction is found by dividing the actual thickness by the apparent thickness. It is often not possible to make the readings with the designated accuracy (0.001 inch) because severe spherical aberration, requiring that the cone of illumination be cut down, is encountered. Under these circumstances the accuracy may fall to ±0.04. (16).

PREFERRED METHODS FOR DETERMINING REFRACTIVE INDEXES OF SPECIFIC POLYMERS

Several tables of values of refractive indexes of polymers have been prepared (5, 10, 23, 24, 36, 41); they include values for

many polymers for which there is no published discussion of the method used in determining the values cited. Those determinations that have been described are listed in Table I along with an approximate statement as to the accuracy achieved. This information is rather meager in view of the many possible types of polymers and, furthermore, undoubtedly needs some revising. For the many types for which no information is available, the following generalizations can be followed in selecting a method to be tried.

If the polymer is soft or becomes soft on heating to 70° C. or below, a film of the polymer can be mounted directly or on a flat. If soluble, cast films can be prepared on the prism or preferably on flats to be attached to the prism. If hard and brittle, a polished block can be prepared for grazing incidence observation. If of the infusible type, it is necessary to prepare a machined or molded (in manufacture) piece for examination by total reflection or grazing incidence. If opaque, only total reflection can be used but is not always operable.

Of the types of illumination in critical angle measurements, ease of observation usually decreases in the order: transmitted, grazing incidence, and reflected light. Polymers that are soluble and low softening require special contact liquids and often none is known. Such polymers are, for that same reason, not usually examined by immersion. Conversely, polymers that are insoluble or infusible are often best examined by immersion. A specific recommendation as to the best method for a given polymer type is not always possible because variations in molecular weight and cross-linking alter fusibility and solubility so as to limit the choice of methods.

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Measurement of Adherence of Organic Coatings to Metal Surfaces

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This paper describes an instrument and a method of measuring the adherence of organic coatings to metal surfaces. The property of adherence, as used here, is not synonymous with the term "adhesion." Adherence is derived from a number of factors, of which adhesion is but one. The other factors include plastic resistance to flow, tear resistance, and mechanical entrapment of the coating in the roughness of the metal surface.

THE measurement of adherence (usually called "adhesion") has never been easy. Work and Leigh (3) classify the methods of adherence measurements into five categories: (1) tensile methods, (2) scratching or gouging tests, (3) base deformation tests, (4) impact tests, and (5) miscellaneous tests. The history and development of these methods have been reviewed by others (4). It is the authors' desire to describe their own development of one method that they feel has possibilities for ready application to plant and laboratory work. That method is a "scratch test," but because the scratch is made with a knife edge 4 mm. wide the result is a band and not a narrow groove such as would be made with a needle point. Koenig (1), Koole (2), and Rossmann (5) investigated the possibilities of the knife-edge scratch tester; each approached the subject from a viewpoint differing somewhat from the others. The present authors' development, while basically the same as the others, differs substantially in many essential details.

ADHERENCE TESTER

The tester consists of a plate, E (Figures 1 and 2), on which is fastened the metal base plate, V, containing the coating to be tested. By means of the motor, A, the plate moves in the direction of the arrow, pulling the base plate under a weighted knife-edge, G, which is connected by means of the beam, P, and the wire, Q, to the pendulum, L. E is supported by the carriage, F, which is moved forward by means of the worm screw, C, and the threaded supports, D, D.

P is supported by the device, N, which rotates about the axis, I. As G moves forward with the base plate containing the coating, the pendulum weight, M, is raised. This procedure produces a backward pull on G. At the moment the backward pull equals the forward thrust exerted by the coating, the knife begins to remove the coating. From here on G and M remain stationary while E

continues to advance. When this happens a reading is taken on an Ames scale, K, which has a sliding arm, W, resting on and activated by an eccentric, X. The scale reading is a function of the distance through which M has been raised.

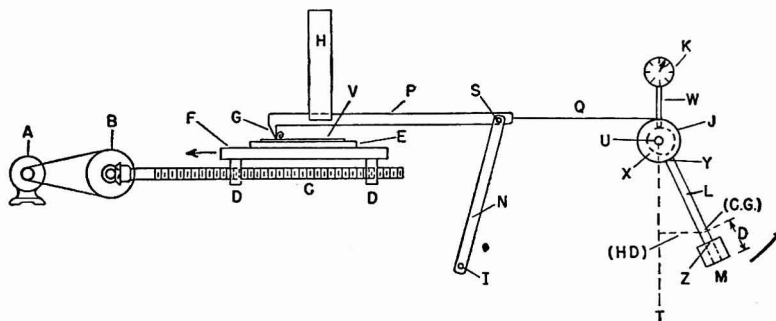As the knife is on a beam pivoted at S, and swings freely on this

Figure 1. Adherence Tester

pivot, a pressure weight, H, is necessary to keep the knife-edge down in contact with the base plate. This produces friction, which must be subtracted from the original reading. To do this a blank is run. The base plate is, therefore, returned to its original position and a run is made on the base metal strip—that area previously occupied by the coating. Both readings are converted to dynes and the second reading is subtracted from the first. The difference is the stripping force, SF.

In order to convert Ames reading to dynes, it is necessary to know the position of the center of gravity, CG of the pendulum, the pendulum weight, and the horizontal distance, HD, between CG and the vertical, T. The pendulum is composed of a bar and a number of weights that can be fastened to it in various combinations. The equation that gives the distance, D, from the lower end of the bar to the center of gravity is (densities of the bar and weight are assumed equal)

$$D = \frac{a^2bc - d^2ef}{2(abc + def)} \quad (1)$$

The weight is flush with the lower end of the pendulum bar, a, b, and c (not marked in Figure 1) are the dimensions of the weight, a being the length of the edge parallel to the length of the bar. d is the "length" of the bar and e and f are its other linear dimensions. As the bar lies across the wheel, J, the correct length, d, to be used for CG determinations is, in this case, the distance from the circumference, Y, of the wheel to the upper surface Z, of the pendulum weight. If D is found to be positive, CG is above the weight; if negative, it is inside the weight.
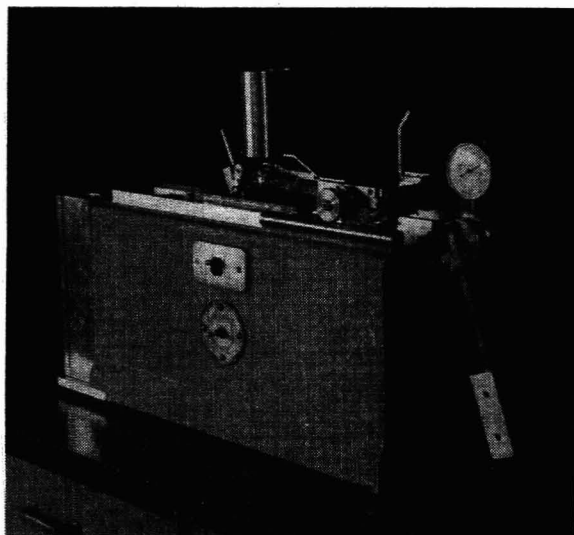
Figure 2. Adherence Tester

After the centers of gravity of the various pendulum-weight combinations are obtained, interpolation curves (Figure 3) are drawn by plotting HD vs. Ames reading. In order to convert HD to dynes, it is necessary to multiply it by an instrumental constant. This constant, K, is calculated as follows:

At equilbrium (Figure 4) the torque to the left of the axis, U, equals the torque to the right. Then,

$$W_1R_1 = W_2R_2 \qquad (2)$$

where W_1 is the force exerted in removing the coating and in overcoming the frictional resistance of the knife-edge against the plate. R_1 is the radius of wheel J. W_2 is the force (a component of the weight of the pendulum) that is exerted perpendicularly to the length of the pendulum. R_2 is, in this case, the effective length of the pendulum and is measured from the axis, U, to the center of gravity, CG. In order to solve Equation 2 for W_1, it is necessary to re-write W_2R_2 in terms of HD and the pendulum weight, W_P.

In Figure 5 triangles abc and $a'b'c'$ are similar. Then, if vector a is the weight of the pendulum, c will be the driving force, W_2, perpendicular to the pendulum arm. It follows that

$$ca' = c'a \qquad (3)$$

But

$$ca' = W_2R_2$$

and

$$c'a = (HD)W_P$$

Therefore

$$W_2R_2 = (HD)\, W_P$$

but

$$W_2R_2 = W_1R_1$$

Therefore

$$W_1R_1 = (HD)\, W_P$$

Converting to dynes and rearranging gives

$$W_1 = \frac{980\, W_P}{R_1}\ (HD) \qquad (4)$$

or

$$W_1 = K(HD) \qquad (5)$$

K is the pendulum constant.

Because W_1, in Equation 5, contains the force necessary to overcome the friction of the knife-edge against the plate, this factor must be eliminated in order to obtain the true stripping force of the coating. This cannot be done by subtracting the Ames scale reading of the blank from the scale reading of the test run because the Ames gage reading does not bear a linear relationship with HD. The HD corresponding to the Ames gage readings is obtained from the calibration curves, Figure 3.

Let $W_1 = (SF) + (FF)$ where (FF) is the frictional force; then

$$(SF) + (FF) = K(HD)_T \qquad (6)$$

and

$$(FF) = K(HD)_B \qquad (7)$$

Subtracting,

$$(SF) = K[(HD)_T - (HD)_B] \qquad (8)$$

where $(HD)_T$ and $(HD)_B$ are the horizontal distances, respectively, of the test run and of the blank.

Knife and Jig. The first experiments were made with steel knives on glass and on steel plates. The results were not good, for the knife-edge invariably caught in these surfaces and thus interrupted and destroyed the value of the measurements. This situation continued for some time before it became apparent that the secret of a successful tester of the knife type lay in the use of a relatively soft knife rather than in a hard steel one. Knives were then made of a great variety of materials and tried out. Plastics did not prove satisfactory, as their lack of macroscopic structure allowed the thin edge of the knife to curl. The most satisfactory materials are substances like ivory; mahogany, ebony, and other hard woods were also found satisfactory. Ivory, however, proved to be the most serviceable of the lot. All the data reported below were obtained with ivory knives.

SHARPENING THE KNIFE. The knife-edge must be sharp, straight, have no rounded corners, and must possess no signs of burrs and nicks. By "sharp" is meant an edge so narrow that it looks like a thin line at a magnification of 150 diameters. By "straight" is meant there should be no deviation of more than 2 microns from a mathematical straight line. If the knife is 4 mm. wide, the corners should be sufficiently square so that the strip removed from the coating is clean-cut on both sides and 4 mm. in width as far as can be determined with a hand lens and a good ruler.
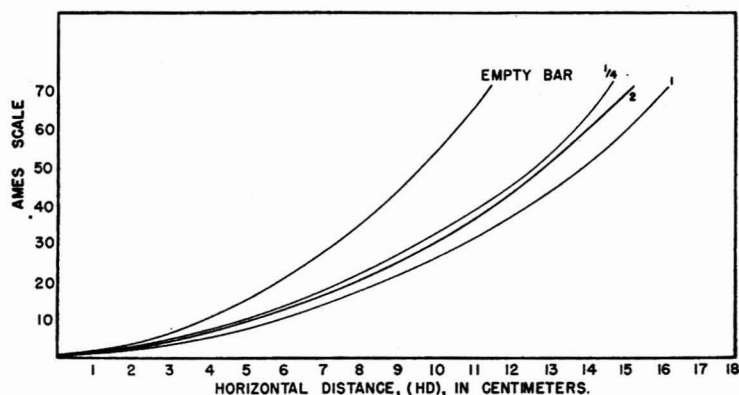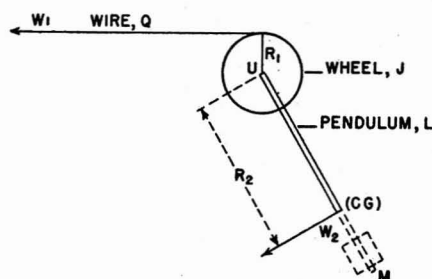

Figure 3. Interpolation Curves

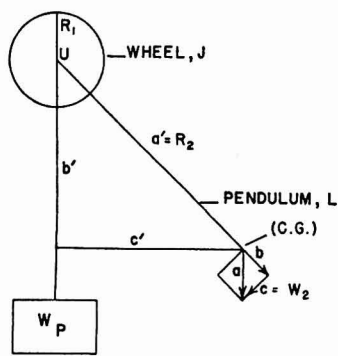**Figure 4. Diagram of Forces**
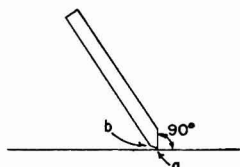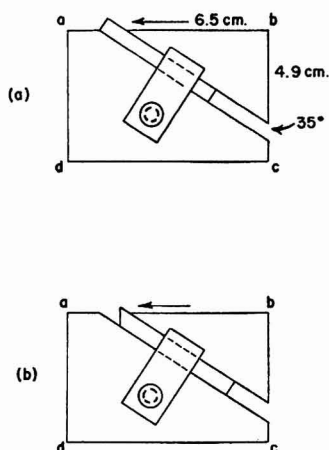
Figure 5. Vector Diagram

Figure 6. Knife

Figure 7. Knife

In order to carry out the above requirements, it is necessary to hold the knife in a jig during sharpening (Figure 6). Two faces are cut while the knife is in the jig. The intersection of these faces is the line which forms the edge of the knife. The jig is a steel block approximately 6.5 × 4.9 × 3.6 cm. In the 6.5 × 4.9 face is cut a slot which holds the knife. The angle that this slot makes with the grinding face of the block is 35°. Across the block is clamped a metal strip which holds the knife in a firm position (Figure 6, a). The first face is cut by rubbing the ab face of the block on emery paper, using first No. 1 then No. 4 grit and rubbing always in the direction of the arrow.

When the first face is finished and polished (with the No. 4 grit), the knife is turned 180° around its long axis to position b, Figure 6. A small face is now cut on the tip in the same manner that the first face was produced. This will give a knife shaped as shown in Figure 7. a is called the "toe," and b is called the "heel" of the knife. The first face is placed in the tester in such a way that it makes an angle of approximately 90° with the coating. At this angle the vertical component of the cutting force is zero, and the entire applied force is parallel to the surface of the plate.

PREPARATION OF PLATE AND COATING. The plate is of metal (never glass or wood), and for convenience of fitting into the adherence tester, its size has been made 5 × 11.25 cm. (2 × 4.5 inches). The thickness of the plate is immaterial, as long as it can be cut readily and retains its flatness. The cleanliness or condition of the plate surface can be whatever the investigator chooses to have and is capable of producing. In order that the knife may rest on the plate and not on the coating, the upper edges of the plate is treated with a softener or solvent that will permit the removal of a small strip of the coating (see Figure 8). The knife-edge is then set on this strip and the plate moved against it. Such a method eliminates the necessity of pushing the knife-edge through the coating, a procedure that invariably dulls the edge. In the adherence tester shown in Figure 1 the metal plate is fastened by means of adhesive tape to a removable block, E. The tape is run around the edge of the plate. More convenient methods can be devised for clamping the plate to the tester.

The plate is wide enough to permit making seven parallel cuts along its length separated by a width of coating about 2 mm. wide (Figure 8). The film thickness is measured from the top surface of the narrow uncut strip to the surface of the bare metal plate adjacent to it. In the work described in this paper, all film thickness measurements were made with a Carson electronic micrometer, which gives results in mils. Since "mil" is customarily employed throughout the coating industry, it has been retained here as the unit of film thickness, even though SF/width is recorded in the metric system.

Principles Involved in Measurement of Adherence. In removing coatings by means of the adherence tester, certain elementary principles exist. For thin films where the tear resistance is negligible, SF divided by the strip width is a constant. Laboratory data proving the correctness of this conclusion are given in Table I. The first strip was cut with the full 4-mm. width of the knife-edge. The other widths were produced by trim-

ming off the corners of the knife. The results of the various cuts gave the panel the appearance shown in Figure 8, lower. The stripping force divided by the strip width, SF/width, is called the stripping force per unit width and is given in dynes per centimeter.

SF/width is independent of the pressure weight (H, Figure 1). The pressure weight increases the friction on the base plate, giving a higher scale reading, but it also gives a proportionately higher blank reading. The result is that there is no effect on the ultimate value of SF/width (Table II).

Data for the third principle—the adherence measurement is independent of speed—are given in Table III. The speed is the length of strip removed per second.

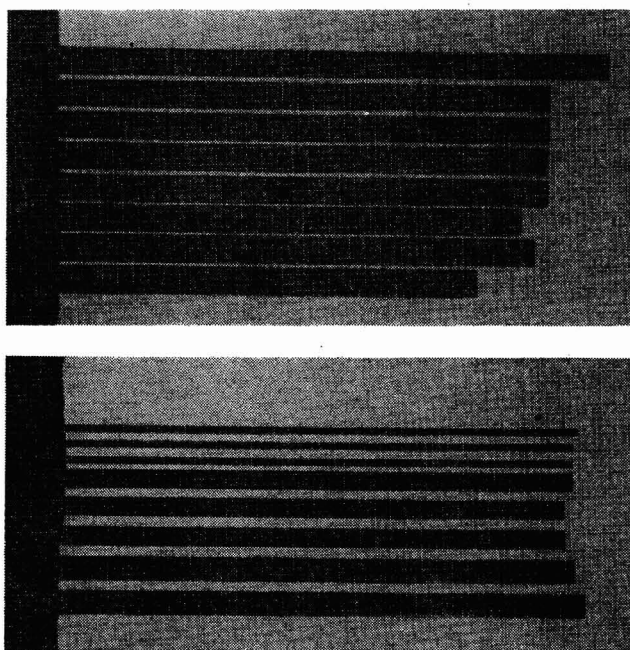SF/width is independent of the weight of the pendulum (Table IV).

Figure 8. Preparation of Plate and Coating

Table I. Constancy of SF/Width

Width of Strip Mm.	Panel	SF/Width Dynes/cm.
4.0	A	160 × 10⁴
3.3	A	160
1.0	A	161
3.6	B	135
2.5	B	138

Table II. Pressure Weight Does Not Affect SF/Width

Pressure Weight Grams	Panel	SF/Width Dynes/cm.
2079	A1	150 × 10⁴
1255		150
2079	A2	168
1255		168
3076	A3	154
1679		154
3076	B1	90
1679		93

Table III. Independence of Speed and *SF*/Width

Speed Cm./sec.	SF/Width Dynes/cm.
0.11	107 × 10⁴
0.21	114
0.37	117
0.42	116
0.46	109
0.69	104

Table IV. Independence of Pendulum Weight and *SF*/Width

Pendulum Weight Grams	Panel	SF/Width Dynes/cm.
522	C	143 × 10⁴
1042	C	139
522	D	98
261	D	99

Table V. Clear Linseed Modified Alkyd

Panel	ISF, Dynes/Cm./Mil
1	2685 × 10³
2	2953
3	2803
4	2588
5	2779
6	3027
7	2921
8	3000
9	2848
10	2883

The fifth principle, unlike the preceding ones, introduces a nonlinear relationship. This relationship cannot be stated in any simple manner and is presented here in the form of a graph (Figure 9). The curve is produced by plotting film thickness against *SF*/width. The lower part of the curve is, for most practical purposes, linear.

The curve is the result of many measurements made with the same coating material, but employing numerous panels with various film thicknesses. The nonlinear form of the curve probably arises from the fact that corrections have not been made for tear resistance and for a constant adhesion factor. Moreover, in baking thick films, vapor bubbles are produced between the plate and the coating. Such vapor formation would decrease the adhesion.

Assuming that measurements are confined to the lower end of the *SF*/width–film thickness curve, the following approximate equation can be written from the five principles given above:

$$(ISF) = K \frac{(HD)_T - (HD)_B}{WT} \qquad (9)$$

(*ISF*) is the intrinsic stripping force, *W* is the width of the strip removed, and *T* is its thickness. Neither speed nor pressure weight enters the equation (Table V).

One variable about which very little has been said is the angle the cutting face of the knife makes with the metal plate. There will be a marked difference in the measurement, if this angle is allowed to vary over an arc of 20° or more. It is, therefore, well to standardize the angle. The authors use 90 ± 10°. Within this limit, the externally applied force is used mainly in overcoming the force required to strip the coating from the plate.

Effect of Base Plate on *SF*. Because adhesion is a mutual attraction between two different materials, it is natural to expect a difference in adherence measurements from the same material when coated on different base metal plates. The data presented in Table VI show definitely that the adherence of a given material will vary with the nature of the base plate.

Coefficient of Variation. In Table VII is given a series of measurements made with two different coatings for the purpose of determining the precision of the adherence tester. The co-
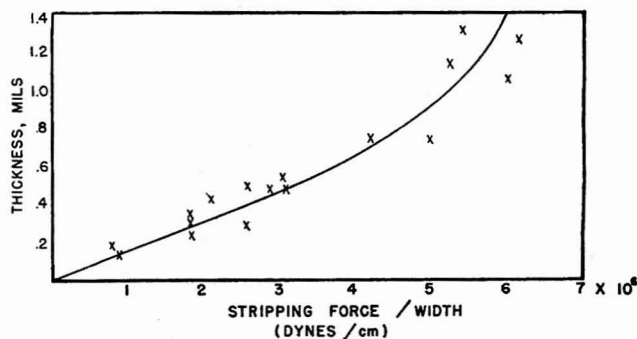
Figure 9. Relationship of Film Thickness and *SF*/Width

efficient of variation is given for each plate and indicates the precision of the instrument. Each cut is read at two different places and averaged. The average coefficient of variation indicates the precision obtained for a number of panels of the same coating and base plate.

Table VI. Data for Three Coating Materials on Different Plates

Metal Base	Stripping Force, Dynes/Cm.		
	A	B	C
Al-Mg alloy	415 × 10⁴	161 × 10⁴	327 × 10⁴
Bonderite	371	300	427
Cold rolled steel	371	238	317
Galvanized iron	318	275	278
Copper	334	227	314
Stainless steel	231	263	326
Chrome plate	271	168	262
Nickel	249	223	182
Brass	279	109	203
Zinc	159	153	108
Electrolytic zinc	225	139	369

Cohesion. Because "adherence" has been arbitrarily defined in this work, the question arose as to inclusion of cohesion in the factors comprising that property. The authors feel that this question constitutes a major point, and due consideration was given to it in the selection of the type of instrument employed. Cohesion is the adherence of a material to itself, and its measurement, obviously, is not involved in the separation of a coating from the surface to which it is adhering. At no time, then, should the instrument allow cohesion to enter the measurement unless its magnitude can be determined and deducted from the total measurement. As an example, in "tensile" tests where the coating cements two plates together, the "break" might occur through the body of the coating rather than at the interface between coating and plate. If such should be the case, the measurement would be related to cohesion rather than to adherence. The instrument that seems to have the best possibilities of eliminating trouble of this nature employs a knife for removing a substantial strip of the coating from the surface.

At the edge of the knife, the coating tears. The resistance to tearing originates in the cohesion of the material. Even the knife type of tester cannot completely avoid the inclusion of cohesion; however, the amount of tear resistance can, in this case, be measured and deducted, if its magnitude warrants such a procedure. The work is carried out as follows:

A strip is cut in the normal manner. This gives a stripping force which includes the tear resistance from the two edges of the strip. A second strip is now cut by moving the knife over the uncut portion of the coating until the cut edge is reached by the far edge of the knife. The second strip will have only one new edge subject to tear resistance.

There are now two readings, one containing the tear resistance from two edges; the other, the tear resistance from a

Table VII. Coefficient of Variation

Panel	No. of Cuts	Average of Readings	Standard Deviation	Coefficient of Variation, %
		Gray Pigmented Alkyd		
1	3	2.97	0.1775	6.0
2	5	3.04	0.1086	3.6
3	5	3.40	0.1633	4.8
4	4	2.88	0.1442	5.0
5	6	2.50	0.1171	4.7
6	5	2.93	0.1858	6.3
7	6	3.04	0.0906	3.0
8	5	3.14	0.1250	4.0
9	4	2.72	0.0912	3.4
			Av.	4.5
		Clear Linseed Modified Alkyd		
1	5	2.48	0.0721	2.9
2	5	2.77	0.0566	2.1
3	5	2.73	0.0245	0.9
4	5	2.52	0.0872	3.5
5	5	2.39	0.0678	2.8
6	5	2.57	0.0748	2.9
7	5	2.59	0.0866	3.5
8	5	2.70	0.1225	4.5
9	5	2.49	0.0927	3.7
10	5	2.56	0.1040	4.7
			Av.	3.2

single edge. Subtracting these gives the tear resistance for a single edge. Multiplying this remainder by 2 gives the total tear resistance. If this result is substantial, it can be subtracted from the stripping force, and thus eliminate cohesion completely from the adherence measurement.

The authors feel that such a procedure is unnecessary where the film thickness is of the order of a few tenths of a mil. Corrections of this kind were not made in the data given in the above tables. Because tear resistance can be made practicably negligible (or can be corrected for if desired) when the knife-edge adherence tester is employed, this type of apparatus was considered to be the best for carrying out the work described in this paper.

SUMMARY AND CONCLUSION

An instrument is described for measuring the adherence of organic coatings to flat metal plates. The plates used do not include the softer metals such as tin, aluminum, and magnesium. The apparatus is of the knife type, which cuts and pushes off a strip of coating of substantial width. The force necessary to do this is calculated in dynes and divided by the strip width to give a ratio called the stripping force per unit width. When this value is

divided by the film thickness, the result is called the intrinsic stripping force. Such measurements are independent of the speed at which the cut is made and of the amount of friction developed by the pressure weight used in forcing the knife-edge into contact with the plate. A chart that shows the precision of the instrument is included.

The adherence tester involves no new basic ideas. A number of investigators have worked with similar apparatus. One development, however, is perhaps novel and deserves consideration—the fact that the instrument uses relatively soft knives, so that the knife will not cut into the metal base plate. The best material for this purpose is ivory, although hard woods can also be used with success. The knife must be harder than the coating—i.e., hard enough to strip the coating—and yet sufficiently soft not to cut into the metal base plate.

The authors believe that the adherence tester can play a serviceable part in the coating industry; and that its field of usefulness can be extended to include soft metals and coated plates that have been strained and distorted.

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SPIRIT BEVERAGES

Determination of Alcohol Content by Volume at 60° F.

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L ARGE quantities of alcoholic beverages imported into this country annually consist chiefly of wines and liquors which are subject to customs duty and internal-revenue tax. The amount of the duty and tax depends in part on the percentage of ethyl alcohol by volume or the true proof; the latter is twice the percentage of ethyl alcohol by volume at 60° F. In this paper, alcohol means ethyl alcohol, percentage (%) means percentage by volume, proof means true proof, and specific gravity means apparent specific gravity, unless otherwise qualified.

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The alcohol content of wines and spirits is usually found by determination of the specific gravity of the product or of a distillate thereof. The latter is necessary if interfering substances such as sugar, glycerol, wine solids, etc., are present. These substances alter the specific gravity of mixtures of alcohol and water—for example, sucrose dissolved in an alcohol-water mixture containing 50% alcohol will increase the specific gravity about 0.0004 for each 0.1 gram of sucrose per 100 grams of mixture; this is equivalent to about 0.20% alcohol.

If the product contains no interfering substances the percentage of alcohol can be determined from the specific gravity of the prod-

The method used in the Bureau of Customs laboratories for determining the percentage of alcohol by volume at 60° F. in wines and in spirit beverages containing interfering substances is based on distillation of all the alcohol in a sample portion, determination of the apparent specific gravity of the distillate, and use of a table prepared by the National Bureau of Standards. The specific gravity preferably is determined at 60° F.; because this is not always practicable, provision has been made for making the determination at any one of several temperatures ranging from 15.56° C./15.56° C. to 35° C./ 35° C., inclusive. For samples not exceeding 70% alcohol by volume the volume of the distillate must be the same as that of the sample portion when both are measured at a predetermined temperature. On samples containing 50 to 70% alcohol, the use of sodium chloride as a distillation aid is recommended. When the sample portion and the distillate are measured at a temperature other than 60° F., the coefficient of expansion of sample and undiluted distillate are assumed to be the same. The procedure for samples containing more than 70% alcohol by volume requires that the volume of the distillate be about twice that of the sample portion. It includes a table and formula for use in correcting for variations in coefficient of expansion of sample and diluted distillate when the sample portion and distillate are measured at a temperature other than 60° F. The formula assumes that the coefficient of expansion of the sample is the same as that of an alcohol-water mixture having the same percentage of alcohol by volume. Experimental data show the relative accuracy and precision of each procedure.

uct and suitable tables. Other methods used in the determination of the alcohol content of such products employ the refractometer (2, 4) or spirit hydrometers (7). In the case of products containing interfering substances, all three methods can be used if all the alcohol in a sample portion is distilled.

Because the Bureau of Customs is charged with the responsibility of determining both the duty and the tax on imported alcoholic beverages, the Division of Laboratories studied the methods in an endeavor to eliminate existing errors and to increase the accuracy. As a result of this investigation an improved method was devised and in 1941 introduced into the customs laboratories. This method was revised in 1943 and again in 1945. The 1943 revision (10) served as a basis (13) for the current official A.O.A.C. procedures (5) for the determination of the alcohol content of distilled liquors. The essential features of the 1941 method and its subsequent revisions are explained in this paper and the more important of the experimental data relating thereto are included.

CONVENTIONAL METHOD

Prior to publication of the sixth edition of the methods of analysis of the A.O.A.C., all distillation procedures referred to in the literature for the quantitative determination of alcohol in beverages containing over 20% alcohol were "dilution" procedures—that is, they required that the volume of the distillate be greater than that of the sample. This requirement was based on the belief that it was inadvisable to permit the percentage of alcohol in the distillate to exceed 20. A typical older procedure (2) specified distilling a 25-ml. sample measured at a known temperature, making the distillate to 100 ml. at the same temperature, and determining the specific gravity of the distillate at one of the temperatures listed in Table 19 (3). It also required that the percentage of alcohol in the distillate be obtained from Table 19 and multiplied by 4 to give the percentage of alcohol in the sample.

When the dilution procedure is used on spirits, the sample and distillate are generally measured at a temperature materially different from the standard temperature for spirits (60° F.). By this procedure the normal experimental errors are multiplied and more serious errors may be introduced because the coefficient of expansion of a diluted distillate will generally differ from that of the sample (12). Although the errors inherent in the dilution procedures were discussed rather thoroughly by Cartwright (12) in 1942, they had been under consideration and largely eliminated prior to that time by the Bureau of Customs (9).

CUSTOMS METHOD, 1941

In the investigations carried out in the customs laboratories prior to adoption of the 1941 method, experiments were conducted in which larger samples were taken; this gave distillates of higher alcohol content than the conventional 20% by volume. The results obtained indicated that distillates of concentrations of 55% or even higher were permissible, provided certain precautions were observed.

Basis. The 1941 method, which was issued in August of that year, included two procedures, one for samples containing not over 55% alcohol, the other for samples of higher concentration. The volumetric glassware consisted of 100-ml. pycnometers, calibrated at the temperature of the determination to eliminate errors due to use of conventional volumes. For samples containing not over 55% alcohol the same pycnometer was used for measuring the sample, receiving the distillate, and determining the specific gravity. The essential differences in the procedure for stronger spirits were greater dilution of the sample in the distilling flask and the use of two calibrated pycnometers for collection of the larger volume of distillate and the subsequent determinations of specific gravity. The procedure for samples containing over 55% alcohol was abandoned when the method was revised in 1943, and is not referred to further in this paper.

The 1941 method for samples containing not over 55% alcohol was based on the specific gravity of the distillate when all the alcohol in 100 ml. of the sample measured at a predetermined temperature was distilled and the distillate was brought to the same volume at the same temperature. It required that the specific gravity be obtained at the predetermined temperature, which was one of the temperatures listed in Table 19 (3), by dividing the apparent weight of the distillate at the temperature by the apparent weight of an equal volume of water at the same temperature. The corresponding percentage of alcohol at 60° F. was then obtained from the table.

When the sample portion and the distillate were measured at a temperature other than 60° F., the coefficients of expansion of sample and distillate having the same alcohol concentration were assumed to be the same. Although the assumption is not theoretically correct, it applies in the case of the present customs procedure (11) for samples containing not more than 70% alcohol and to the official A.O.A.C. procedure (5) for the percentage of alcohol in samples containing not more than 60% alcohol. The extent of the error resulting from this assumption has not been thoroughly investigated because it varies with the alcohol content of the product and the quantity and nature of the interfering

substances. However, in the case of a typical imported brandy containing 53.7% alcohol and a relatively high amount of non-volatile matter (1.27 grams per 100 ml.) the authors estimate that, if the measurements were made at 25° C., the error would be materially less than 0.01% alcohol. This estimate is based on experimental data obtained in a study of the coefficients of expansion of the brandy and of an alcohol-water mixture having the same alcohol content by volume. The error, of course, can be eliminated by measuring the sample portion and the distillate at 60° F.

Precautions. The 1941 method stressed the necessity for taking precautions to prevent loss of alcohol and to eliminate undesired substances from the distillate.

Specifically, it required that the volume of the sample portion and the distillate be the same, that they be measured at the same temperature, and that this temperature be accurately known and controlled (±0.1° C.) by means of a constant-temperature bath; that the inside of the distilling flask be wet prior to introduction of the sample; that the joints between the connecting bulb and the distilling flask and condenser tube be tight; that about 96 ml. of distillate be collected in the pycnometer in which the sample was measured; that the condenser water be as cool as practicable; that at the start of the distillation the pycnometer be partly immersed in ice or ice water to keep the distillate in the pycnometer at a temperature below 20° C.; that the distillation be at a uniform rate and take not less than 30 nor more than 60 minutes; that the distillate be homogeneous after it was made to volume but that in mixing none of the distillate be allowed above the 100-ml. mark of the pycnometer; and that a test be made after distillation to determine whether or not all the alcohol had been distilled from the sample.

Equipment. The original specifications for equipment in the 1941 method were carried over into the 1943 and 1945 revisions, and they appear in some detail in the official A.O.A.C. procedure (5). The 100-ml. pycnometer is generally similar to that described by Brinton (6).

CUSTOMS METHOD, 1943

Experimental work conducted by the Division of Laboratories following issuance of the 1941 method indicated that samples of higher alcohol per cent could be tested, provided the volume of liquid remaining in the distilling flask, at the end of the distillation, was a minimum. This condition was obtained by adding as little wash water as practicable to the contents of the distilling flask, prior to distillation. The experimental work also resulted in the development of a dilution procedure which was more practicable than that described in the 1941 method. The "new" dilution procedure more closely resembled the conventional dilution procedures, but provided corrections for volumetric errors and the usual errors due to variations in coefficient of expansion of alcohol solutions of various concentrations.

These improvements were incorporated in a revised method which was issued to customs officers in October 1943 (10). In the revision, the maximum percentage of alcohol permissible in the distillate was fixed at 50; this was considered temporary, however, pending the outcome of further study of the question. The original specifications for equipment were expanded to include a calibrated 50-ml. pycnometer.

Procedure A. The 1943 revision contained only one material change in the procedure for samples containing 50% or less alcohol, as compared with the 1941 procedure. The change involved a reduction from 150 to 125 ml. in the total volume of liquid permissible in the distilling flask at the start of the distillation, except that a greater volume was permissible in the case of samples containing excessive amounts of nonvolatile matter.

Procedure B. The 50-ml. pycnometer specified in the 1943 method was similar to the type used in the Laboratory Division, Bureau of Internal Revenue, U. S. Treasury Department, Washington, D. C. (5). This pycnometer was intended for tentative use in customs laboratories when the alcohol content of a sample exceeded 50%. The procedure for this purpose, referred to

henceforth as Procedure B, provided that the sample be measured in the calibrated 50-ml. pycnometer; that the total volume in the distilling flask prior to distillation be 125 ml., except as indicated in the preceding paragraph; and that the distillate be collected in one of the calibrated 100-ml. pycnometers. It also provided a table and formula for use in correcting for differences in coefficient of expansion when the sample portion and the diluted distillate were measured at 20° or 25° C. instead of at 60° F., the standard temperature. (Corrections for other temperatures are provided for in Table 8 of the Customs Gauging Manual, 8.) When the sample portion and the distillate are measured at a temperature other than 60° F., it is assumed that the coefficient of expansion of the sample is the same as that of an alcohol-water mixture having the same alcohol content. The official A.O.A.C. procedure for samples containing more than 60% alcohol requires that the sample portion and the distillate be measured at 60° F. This requirement is theoretically correct, but it is not always practicable.

The following formula illustrates how the percentage of alcohol is computed when Procedure B is used and the sample portion and distillate are measured at a temperature other than 60° F.

$$S = \frac{D \times W}{W'} \times \frac{M}{M'} \tag{1}$$

where
S = % alcohol at 60° F. in sample
D = % alcohol at 60° F. in distillate
W = apparent weight, in grams, of water contained in the 100-ml. pycnometer when made to mark at 20° C.
W' = apparent weight, in grams, of water contained in the 50-ml. pycnometer when made to mark at 20° C.
M = factor for converting volume of distillate from 20° C. to 60° F.; see Table VIII.
M' = factor for converting volume of sample portion from 20° C. to 60° F. (see Table VIII); % alcohol assumed to be twice that of distillate.

(The factors M and M' are based on experimental work performed by the National Bureau of Standards, 14.)

EXPERIMENTAL

Following issuance of the 1943 revision of the customs method, three separate studies of the revised method were initiated by the Division of Laboratories. Before the first study was started, however, the method was modified by reducing the total volume permissible at the start of the distillation to 120 ml., because preliminary work indicated that it would result in more complete recovery of the alcohol. In most cases, a majority of the nine customs laboratories participated in the experimental work incidental to the three studies. In each case determinations were made in quintuplicate by each participating laboratory. Standard methods were used in evaluating the data (1).

First Study. In the first study the five determinations in a laboratory were run simultaneously.

EXPERIMENT I (to determine whether Procedure A could be used on samples containing as much as 70% alcohol).

Each chemist prepared pure alcohol-water solutions containing approximately 60 and 70% alcohol (solutions I and II, respectively). After the solutions had stood at least 24 hours, each chemist determined the specific gravity of each solution at 20° C./20° C., using calibrated 100-ml. pycnometers, and the per cent alcohol at 60° F. The sample was measured at 20° C. in the 100-ml. pycnometer and transferred quantitatively to the distilling flask, using 20 ml. of wash water; the alcohol was distilled into the same pycnometer and made to mark at 20° C.; and the specific gravity of the distillate at 20° C./20° C. and the % alcohol at 60° F. were determined.

Conclusions. The data are summarized in Table I. Assuming that the values in columns I represent the actual percentages of alcohol in the samples, it appears that Procedure A is capable of yielding accurate results on solutions containing as much as 70% alcohol. The average standard deviations ($\bar{\sigma}_5$) before and after distillation indicate that, on such solutions, Procedure A is

Table I. Summary of Data on Accuracy and Precision

[Procedure A, 1943 revision modified (alcohol-water mixtures, Experiment I, first study)]

Customs Laboratory Symbol	Solutions I					Solutions II				
	% Alcohol at 60° F.[a]			σ_b (in % Alcohol)		% Alcohol at 60° F.[a]			σ_b (in % Alcohol)	
	1. Before distillation	2. After distillation	Difference (1 − 2)	Before distillation	After distillation	1. Before distillation	2. After distillation	Difference (1 − 2)	Before distillation	After distillation
A	61.81	61.75	+0.06	0.031	0.031	72.00	71.67	+0.33[b]	0.033	0.135[c]
B	60.06	60.05	+0.01	0.010	0.014	69.89	69.87	+0.02	0.022	0.029
C	60.57	60.58	−0.01[b]	0.020	0.102[c]	69.69	69.66	+0.03	0.023	0.021
D	60.70	60.71	−0.01	0.026	0.031	70.20	70.20	...	0.013	0.014
E	60.06	60.02	+0.04	0.008	0.013	69.96	69.93	+0.03	0.006	0.008
F	59.72	59.69	+0.03	0.017	0.010	69.52	69.46	+0.06	0.013	0.015
Average			+0.03	0.019	0.020			+0.03	0.018	0.017
Precision[d]	±0.07	±0.07				± 0.06	± 0.06			

a Based on specific gravity at 20° C./20° C.; mean of five determinations.
b Omitted in computed average difference.
c Outside control limits ($B_3\bar{\sigma}_b$ and $B_4\bar{\sigma}_b$); omitted in computing average ($\bar{\sigma}_b$).
d Maximum chance error of single determination under controlled conditions; based on formula $\dfrac{3\bar{\sigma}_b}{c_2}$.

Table II. Summary of Data on Accuracy and Precision

[Procedure B, 1943 revision modified (alcohol-water mixtures, Experiment II, first study)]

Customs Laboratory Symbol	Solutions I					Solutions II				
	% Alcohol at 60° F.[a]			σ_b (in % Alcohol)		% Alcohol at 60° F.[a]			σ_b (in % Alcohol)	
	1. Before distillation	2. After distillation	Difference (1 − 2)	Before distillation	After distillation	1. Before distillation	2. After distillation	Difference (1 − 2)	Before distillation	After distillation
A	61.93	61.57	+0.36[b]	0.120[c]	0.158[c]	72.06	71.81	+0.25	0.041	0.093
B	60.08	60.03	+0.05	0.010	0.039	69.91	69.87	+0.04	0.010	0.051
C	60.48	60.58	−0.10	0.039	0.101	69.64	69.68	−0.04	0.051	0.100
D	60.78	60.62	+0.16	0.010	0.055	70.20	70.13	+0.07	0.026	0.081
E	60.06	60.02	+0.04	0.013	0.037	69.99	69.94	+0.05	0.014	0.039
F	59.73	59.63	+0.10	0.060	0.031	69.54	69.46	+0.08	0.011	0.108
G	60.63	60.43	+0.20	0.042	0.069	70.83	70.78	+0.05	0.030	0.144
Average			+0.08	0.029	0.055			+0.047	0.026	0.088
Precision[d]	± 0.10	±0.20				±0.09	±0.31			

a Based on specific gravity at 20° C./20° C.; mean of five determinations.
b Omitted in computing average difference.
e Outside control limits ($B_3\bar{\sigma}_b$ and $B_4\bar{\sigma}_b$); omitted in computing average ($\bar{\sigma}_b$).
d Maximum chance error of single determination under controlled conditions; based on formula $\dfrac{3\,\bar{\sigma}_b}{c_2}$.

capable of satisfactory precision. The indicated precision of a single determination under controlled conditions, at a probability level of 0.997, is better than ±0.10% alcohol.

EXPERIMENT II (to determine whether Procedure B is as accurate and precise as Procedure A).

The specific gravity of each solution prepared for Experiment I was determined at 20°C./20° C., using calibrated 50-ml. pycnometers, and the per cent alcohol at 60° F. was determined therefrom. The sample was measured at 20° C. in the 50-ml. pycnometer, transferred quantitatively to the distilling flask, using 70 ml. of wash water, and the alcohol was distilled into a calibrated 100-ml. pycnometer and made to mark at 20° C.; the specific gravity at 20° C./20° C. and the % alcohol at 60° F. were then determined. One additional laboratory participated in this experiment.

Conclusions. The data are summarized in Table II. Assuming that the values in columns 1 of Tables I and II represent the actual percentages of alcohol in the samples and comparing the differences (1 − 2) in the two tables, it appears that Procedure A is more accurate than Procedure B even on samples containing 70% alcohol. The average standard deviations ($\bar{\sigma}_b$) after distillation indicate that Procedure A is more precise than Procedure B.

EXPERIMENT III (to determine whether the distillate is homogeneous after it has been made to mark in the 100-ml. pycnometer. This question is important, as a significant error is introduced if the distillate is not properly mixed).

After the apparent weight of the distillate had been determined in Experiment I, the pycnometer containing the distillate was thoroughly shaken; the specific gravity at 20° C./20° C., using the 50-ml. pycnometer, and the per cent alcohol at 60° F. were then determined. Only four laboratories participated in this experiment.

Conclusions. The data are summarized in Table III. The differences (1 − 2) may be compared for significance with the expected differences between duplicate determinations where mixing errors are absent. From the data in Tables I and II ("before distillation") the universe standard deviation of a determination of alcohol content by specific gravity may be computed; $\sigma' = 0.0274\%$ alcohol. At a probability level of 0.997, the maximum difference between duplicate determinations is $3\sigma'\sqrt{2}$, or ±0.116% alcohol, and the maximum mean difference for a set of five such duplicate determinations is $0.116 \div \sqrt{5}$, or ±0.052% alcohol. Only in the case of laboratory A, where the data showed lack of control, was this maximum mean difference exceeded. It may be concluded, therefore, that under best conditions of testing inadequate mixing of the distillate is not an assignable cause of error.

Second Study. The second study was designed to reveal information regarding the precision of the method under routine conditions. For this purpose, samples of two different simulated liquors (solutions III and IV), each containing an appreciable quantity of nonvolatile matter, were employed. Each laboratory ran one determination per day for 5 days; in each case the specific gravity was determined at 20° C./20° C.

EXPERIMENT IV (to determine the precision of Procedure A under routine conditions).

Two simulated liquors containing about 50% alcohol (solution III) and about 85% alcohol (solution IV) were prepared in one of the customs laboratories. Portions of these liquors were sent to each of the other laboratories. Each chemist determined the per cent alcohol at 60° F. in each of the two samples by the modified Procedure A used in Experiment I.

Conclusions. The data are summarized in Table IV. In the case of the liquor containing about 50% alcohol, the indicated precision of a single determination under routine conditions, for a probability level of 0.997, is about ±0.16% alcohol. In the case of the liquor containing about 85% alcohol, the data indicate that modified Procedure A is not sufficiently precise for use under routine conditions.

Table III. Summary of Data on Homogeneity of Distillate

[Procedure A, 1943 revised modified (alcohol-water mixtures, Experiment III, first study)]

Customs Laboratory Symbol	Solutions I, % Alcohol at 60° F.[a]			Solutions II, % Alcohol at 60° F.[a]		
	1. Distillate	2. Distillate after thorough mixing	Difference (1 − 2)	1. Distillate	2. Distillate after thorough mixing	Difference (1 − 2)
A[b]	61.75	61.79	−0.04[b]	71.67	71.80	−0.13[b]
B	60.05	60.04	+0.01	69.87	69.87	0
D	60.71	60.71	0	70.20	70.18	+0.02
E	60.02	60.04	−0.02	69.93	69.94	−0.01

a Based on specific gravity at 20° C./20° C.; mean of five determinations.
b Data for this laboratory exceed control limits.

Table IV. Summary of Data on Routine of Procedure A, 1943 Revision Modified

(Simulated liquors, containing nonvolatile matter, Experiment IV, second study)

Customs Labora-tory Symbol	Solution III				Solution IV			
	% Alcohol at 60° F.[a]		σs (in % Alcohol)		% Alcohol at 60° F.[a]		σs (in % Alcohol)	
	Before distil-lation[b]	After distil-lation	Before distil-lation[b]	After distil-lation	Before distil-lation[b]	After distil-lation	Before distil-lation[b]	After distil-lation
A	48.56	51.75[c]	0.062	0.050	84.06	79.85[c]	0.033	0.401
B	48.54	51.82[c]	0.013	0.075	84.04	84.32[c]	0.012	0.294
C	48.52	51.49[c]	0.058	0.056	83.98[c]	85.01[c]	0.028	0.241
D	48.56	51.54	0.024	0.014	84.04	84.22[c]	0.010	0.135
E	48.55	51.52	0.014	0.019	84.08[c]	83.44	0.008	0.236
F	48.53	51.55	0.038	0.049	84.03	81.55[c]	0.030	0.405
G	48.52	51.46[c]	0.075	0.076	84.04	84.25[c]	0.040	0.066
H	48.58	51.54	0.025	0.035	84.07	84.26[c]	0.013	0.185
I	48.60	51.45[c]	0.022	0.024	84.01	83.86[c]	0.013	0.310
Average	48.55	51.57	0.037	0.044	84.04	83.42	0.021	0.253
Precision[d]	±0.13	±0.16			±0.07	±0.90		

[a] Based on specific gravity at 20° C./20° C.; mean of five determinations.
[b] Apparent % alcohol based on apparent specific gravity of sample.
[c] Outside control limits.
[d] Maximum chance error of single determination based on data in control for σs and formula $\frac{3\bar{\sigma}_s}{c_2}$.

Table V. Summary of Data on Routine Precision of Procedure B, 1943 Revision Modified

(Solution IV, simulated liquor, containing nonvolatile matter, Experiment V, second study)

Customs Labora-tory Symbol	% Alcohol at 60° F.[a]		σs (in % Alcohol)	
	Before distil-lation[b]	After distil-lation	Before distil-lation[b]	After distil-lation
A	84.07	85.80[c]	0.070[c]	0.259[c]
B	84.03	85.94[c]	0.013	0.291[c]
C	84.00	85.19	0.029	0.061
D	84.04	85.22	0.012	0.099
E	84.10[c]	85.30	0.010	0.025
F	84.06	85.27	0.039	0.070
G	84.04	85.05[c]	0.039	0.090
H	84.08	85.29	0.013	0.030
I	84.00	85.29	0.019	0.428[a]
Average	84.05	85.37	0.022	0.063
Precision[d]	±0.08	±0.22		

[a] Based on specific gravity at 20° C./20° C.; mean of five determinations.
[b] Apparent % alcohol based on apparent specific gravity of sample.
[c] Outside control limits; σs based on data in control for σs.
[d] Maximum chance error of single determination based on data in control for σs and formula $\frac{3\bar{\sigma}_s}{c_2}$.

EXPERIMENT V (to determine the precision of Procedure B under routine conditions).

Each laboratory determined the per cent alcohol at 60° F. in the liquor containing about 85% alcohol (solution IV) by the modified Procedure B used in Experiment II.

Conclusions. The data summarized in Table V indicate that the precision under routine conditions, for a probability level of 0.997, is comparable with the precision indicated for Procedure B in Experiment II. When the data in Tables IV and V are considered together, it is evident that Procedure B is more accurate and more precise than Procedure A on liquors containing 85% alcohol.

Third Study. Further study of Procedure A was undertaken with respect to its application to solutions of high alcohol content. Three possible improvements were suggested—namely, addition of salt (sodium chloride) to the distilling flask prior to transfer of the sample, immersion of the flask in ice water during the transfer, and reduction of the rate of distillation. Two experiments in-

volving Procedure A, modified as suggested, are described below.

EXPERIMENT VI (to determine the accuracy of Procedure A as modified on solutions containing about 85% alcohol).

Each chemist prepared a pure alcohol-water solution containing about 85% alcohol (solution V). The per cent alcohol of this solution at 60° F. was determined by modified Procedure A, using 10 grams of salt and without salt. In each laboratory each determination without salt was made simultaneously with a determination using salt.

Conclusions. The data are summarized in Table VI. The average loss of alcohol indicated for Procedure A as modified was 0.94% when salt was not used but only 0.31% when salt was added. On the simulated liquor of comparable strength (solution IV), the indicated loss for Procedure A without salt was 1.95% alcohol (see Tables IV and V). The improvement in accuracy for Procedure A without salt appears to be due to the fact that more attention was given to the distillation rate. Table VI also indicates that the use of salt improved the precision and accuracy of Procedure A.

EXPERIMENT VII (to determine the relative accuracy of Procedures A and B, modified as in Experiment VI).

A simulated liquor (solution VI) containing an appreciable quantity of nonvolatile matter and about 85% alcohol was prepared in one of the laboratories. Each laboratory was furnished with a portion of the liquor. The chemists determined the specific gravity of the distillate at 60° F./60° F. by Procedures A and B, modified as in Experiment VI, except that salt was used only in the case of Procedure A.

Conclusions. The data are summarized in Table VII. In Experiment VI it was found that an average loss of 0.31% alcohol occurred when a solution containing about 85% alcohol was tested by the modified Procedure A with salt. Table VII indicates that the average alcohol content found by the modified Procedure B without salt was 0.21% higher than that found by the modified Procedure A with salt. For spirits containing over 70% alcohol it may be assumed, therefore, that the modified Procedure A is less accurate than modified Procedure B.

PRESENT CUSTOMS METHOD

After completion of the third study, changes suggested therein were incorporated in a revised method which was issued to customs officers in October 1945. A condensed version of this method follows.

Table VI. Summary of Data on Accuracy and Precision of Procedure A, 1943 Revision Modified Further

(Alcohol-water mixture, Experiment VI, third study)

Customs Labora-tory Symbol	Solutions V (without Salt)				Solutions V (with Salt)			
	% Alcohol at 60° F.[a]			σs in % Alcohol after distillation	% Alcohol at 60° F.[a]			σs in % Alcohol after distillation
	1. Before distillation	2. After distillation	Difference (1 − 2)		3. Before distillation	4. After distillation	Difference (3 − 4)	
A	85.36	83.12	+2.24	0.328	85.36	84.53	+0.83	0.419[b]
B	86.23	85.98	+0.25	0.138	86.25	86.13	+0.12	0.059
C	87.56	86.20	+1.36	0.403	87.57	87.41	+0.16	0.184
D	84.78	84.01	+0.77	0.117	84.78	84.67	+0.11	0.098
E	85.14	84.22	+0.92	0.451	85.14	84.94	+0.20	0.023
F	84.99	84.55	+0.44	0.181	85.01	85.02	−0.01	0.012
G	86.14	85.92	+0.22	0.068	86.14	85.57	+0.57	0.149
H	85.07	84.88	+0.19	0.063	85.08	84.97	+0.11	0.029
I	84.23	82.12	+2.11	0.256	84.26	83.59	+0.67	0.149
Average			+0.94	0.223			+0.31	0.088

[a] Based on specific gravity at 20° C./20° C.; mean of five determinations.
[b] Outside control limits ($B_3\bar{\sigma}_s$ and $B_4\bar{\sigma}_s$); omitted in computing average ($\bar{\sigma}_s$).

Table VII. Summary of Data on Relative Accuracy and Precision of Procedures A and B, 1943 Revision Modified Further

(Simulated liquor, containing nonvolatile matter, Experiment VII, third study)

| Customs Laboratory Symbol | Solution VI, Modified Procedure A (with Salt) | | | | Solution VI, Modified Procedure B (without Salt) | | | |
| | % Alcohol at 60° F.[a] | | σ_s in % Alcohol | | % Alcohol at 60° F.[a] | | σ_s in % Alcohol | |
	Before distillation[b]	After distillation	Before distillation[b]	After distillation	Before distillation[b]	After distillation	Before distillation[b]	After distillation
C	84.14	85.07[c]	0.020	0.067	84.12[c]	85.11	0.032	0.043
D	84.16	85.08[c]	0.008	0.055	84.19	85.16	0.008	0.033
E	84.21[c]	84.97	0.008	0.043	84.23[c]	85.21	0.008	0.016
F	84.17	85.23[c]	0.014	0.018	84.18	85.25	0.014	0.064
G	84.20	84.75[c]	0.034	0.090	84.23[c]	85.20	0.073[c]	0.065
H	84.08[c]	85.05	0.014	0.024	84.11[c]	84.98[c]	0.028	0.048
I	84.24[c]	84.56[c]	0.027	0.102	84.19	85.30[c]	0.024	0.211[c]
Average	84.17	84.96	0.018	0.057	84.18	85.17	0.019	0.045
			Precision[d]	±0.07	±0.16			

[a] Based on specific gravity at 60° F./60° F.; mean of five determinations.
[b] Apparent % alcohol based on apparent specific gravity of sample.
[c] Outside control limits; $\bar{\sigma}_s$ based on data in control for σ_s.
[d] Maximum chance error of single determination based on data in control for $\bar{\sigma}_s$ and formula $\frac{3\,\bar{\sigma}_s}{c_2}$.

Apparatus. Essentially similar to that described in (5).

Procedure A. For samples containing 70% alcohol by volume or less:

Use a clean dry 100-ml. pycnometer which has been calibrated at 60° F. Fill to above the graduation mark with the sample and insert the stopper. The liquid in the pycnometer should be free of air or gas bubbles. Immerse in a constant-temperature water bath which is maintained at 60° F., so that the water level of the bath is just above the sample level in the pycnometer. Allow to remain in the bath for 30 minutes. While still at the bath temperature, remove the stopper and withdraw or add small portions of the sample by means of a finely drawn-out glass tube fitted with a rubber bulb until the bottom of the meniscus is just tangent to the graduation mark. Wipe dry the inside neck above the graduation mark, without disturbing the meniscus, using a small strip of filter paper. Stopper and withdraw from the bath.

Transfer the entire contents of the pycnometer to a distilling flask which has just been rinsed with cold water, keeping the flask chilled to ice water temperature during the transfer and rinsing the pycnometer at least three times with a total of 15 ml. of cold distilled water. (In the case of a sample containing alcohol in the range 50 to 70% by volume, add 10 grams of sodium chloride to the chilled distilling flask prior to the transfer.) Add additional distilled water for any sample containing in excess of 5% nonvolatile matter—i.e., sugar—in an amount equal to 1 ml. of distilled water for each additional per cent of nonvolatile matter. Place the rinsed pycnometer in a beaker of ice water, so that it will be immersed nearly to the stem during the distillation period; insert the condenser tube adapter into the neck of the pycnometer and complete the connections. Pass a continuous, rapid stream of cold water through the water jacket of the condenser. Heat the flask rapidly until the liquid reaches the boiling point, then slowly distill at a uniform rate, completing the distillation in from 35 to 60 minutes depending on the alcohol content of the sample.

When the clear distillate measures approximately 97 ml., stop the distillation. Remove the pycnometer from the receiving end of the distilling apparatus and stopper. Mix the distillate thoroughly by swirling. If any drops of distillate are deposited above the graduation mark, wash them down using distilled water. Immerse in a constant-temperature bath at 60° F. and in the manner described above. (At the same time place a small flask containing distilled water in the same constant-temperature bath.) Stopper and allow to remain in the constant-temperature water for 30 minutes. Adjust the meniscus by adding more of the distilled water, using a finely drawn-out pipet, as described above.

Wipe dry the inside of neck above the meniscus, and stopper. Remove from bath and immerse in water at room temperature for a few minutes. Wipe the outside of pycnometer dry with a clean lintless cloth, and allow to remain in the balance room for 15 minutes. Weigh. Obtain the apparent specific gravity of the distillate by dividing the weight of distillate by the water value of the pycnometer. Obtain the corresponding percentage of alcohol by volume at 60° F. from Table 44.23 (5).

Procedure B. Double dilution method for samples containing more than 70% alcohol by volume. Follow the procedure described in Procedure A, with the following modifications:

Adjust the sample to volume at 60° F. by use of a clean dry 50-ml. pycnometer (P_{50}) which has been calibrated at 60° F. and weigh. Add 25 ml. of cold distilled water to the distilling flask. Transfer the entire contents of the pycnometer to the flask and

rinse the pycnometer with portions of cold distilled water measuring 40 ml. in all. Receive the distillate in a 100-ml. pycnometer (P_{100}) calibrated at 60° F. and conduct the distillation as directed under Procedure A above. Obtain the apparent specific gravity of the distillate at 60° F./60° F. and the corresponding per cent alcohol by volume at 60° F. as above. Compute the per cent alcohol by volume at 60° F. in the sample by means of the formula:

$$S = \frac{D \times W}{W'} \tag{2}$$

where S = % alcohol by volume at 60° F. in the sample; D = % alcohol by volume at 60° F. in the distillate; W = water value of P_{100} at 60° F., and W' = water value of P_{50} at 60° F.

Where it is necessary or desirable to measure the sample portion and distillate at 20° or 25° C., in the case of Procedure B, the percentage of alcohol by volume at 60° F. is determined by use of Table VIII and Equation 1: $S = \frac{D \times W}{W'} \times \frac{M}{M'}$.

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Table VIII. Factors for Correcting Percentages of Alcohol by Volume

[From 20° C. or 25° C. to 60° F. (15.56° C.) in equation $S = \frac{D \times W}{W'} \times \frac{M}{M'}$. This table was prepared for use in connection with Procedure B where the sample portion and distillate are measured at 20° or 25° C. The values for M and M' were calculated by use of formula in (14).]

D^a	$\frac{M}{M'}$ 20° C. to 60° F.	$\frac{M}{M'}$ 25° C. to 60° F.	D^a	$\frac{M}{M'}$ 20° C. to 60° F.	$\frac{M}{M'}$ 25° C. to 60° F.
1	1.0000	1.0000	26	1.0016	1.0033
2	1.0000	1.0000	27	1.0016	1.0033
3	1.0000	1.0001	28	1.0015	1.0032
4	1.0001	1.0002	29	1.0015	1.0032
5	1.0002	1.0003	30	1.0016	1.0032
6	1.0003	1.0004	31	1.0015	1.0031
7	1.0003	1.0006	32	1.0015	1.0030
8	1.0004	1.0007	33	1.0014	1.0030
9	1.0005	1.0010	34	1.0014	1.0029
10	1.0005	1.0012	35	1.0013	1.0028
11	1.0007	1.0014	36	1.0014	1.0028
12	1.0008	1.0016	37	1.0013	1.0028
13	1.0009	1.0019	38	1.0014	1.0027
14	1.0010	1.0021	39	1.0013	1.0027
15	1.0011	1.0023	40	1.0013	1.0027
16	1.0012	1.0026	41	1.0013	1.0026
17	1.0014	1.0027	42	1.0013	1.0026
18	1.0014	1.0029	43	1.0013	1.0026
19	1.0014	1.0031	44	1.0013	1.0026
20	1.0016	1.0031	45	1.0013	1.0026
21	1.0016	1.0033	46	1.0012	1.0026
22	1.0016	1.0033	47	1.0013	1.0026
23	1.0016	1.0033	48	1.0012	1.0025
24	1.0016	1.0034	49	1.0012	1.0026
25	1.0016	1.0033	50	1.0013	1.0026

[a] % alcohol by volume at 60° F. in distillate.

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DETERMINATION OF ACETYLENE IN GAS

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A method is described for determining acetylene in gas by scrubbing the gas with a strong solution of silver nitrate and then precipitating and weighing the acetylene complex as $Ag_2C_2.AgNO_3$. The procedure provides for quantitatively removing the acetylene from a flowing gas stream, avoiding the reducing effect of hydrogen upon silver nitrate, and describes a technique for largely avoiding explosion hazards to the operator. As the size of sample is substantially unlimited, the method can be used for determining very low concentrations of acetylene. The accuracy of the method appears to be limited by the mechanical considerations involved in gravimetric procedure.

VARIOUS analytical procedures have been proposed for the determination of acetylene in gas. Sachanen (5) says that present methods are unsatisfactory. Methods depending upon titration of acid liberated by the reaction of acetylene with silver nitrate involve a poor end point and are valueless for gases having a low concentration of acetylene, as, for example, coke-oven gas. Behal (1) suggested gravimetric determination of acetylene by precipitation from a 5% silver nitrate solution in 95% alcohol. Hill and Tyson (2) reported unfavorably upon this procedure. Methods involving precipitation of acetylene with ammoniacal copper solutions are objectionable because, according to Novotny (4) and also Hill and Tyson (2), the ammonia concentration must be maintained, and oxygen and carbon dioxide interfere with the results. The precipitate also is difficult or impossible to remove completely from the absorption tubes.

Because of the extreme insolubility of silver acetylide, it was decided to attack the problem from this point of view and in so doing an interesting phenomenon was observed. When a strong solution such as 35% silver nitrate was used instead of the customary dilute solution, no precipitate was formed initially upon passage of gas containing acetylene. Tests showed, however, that the outlet gas under these circumstances was free of acetylene and that, upon sufficient dilution of the scrubbing reagent, the acetylene was completely precipitated as $Ag_2C_2.AgNO_3$. This strong silver nitrate solution has indeed proved to be exceedingly active in removing acetylene from gas, and the following procedure was devised. It is conveniently independent of size of sample and can therefore be used for analyzing concentrations varying from 100% acetylene to traces. On coke-oven gas carrying 0.05% acetylene, several tests varied among themselves by approximately only 1%. The method also differentiates between acetylene and alkyl acetylenes, as the silver complexes of the latter are apparently not precipitated upon dilution with water. A figure for the alkyl acetylenes could be obtained by subtracting the gravimetric value for normal acetylene from the acidimetric titration value for total acetylenes. While the procedure was evolved for analyzing coke-oven gas it was used satisfactorily on a wide variety of gases. In brief, the method consists in scrubbing the gas with about a 35% silver nitrate solution, usually containing ferric nitrate, diluting this solution highly with water, and filtering, washing, drying, and weighing the residue.

APPARATUS AND CHEMICALS REQUIRED

Three all-glass test-tube scrubbers 25 × 200 mm.; two all-glass test-tube scrubbers 12 × 150 mm.; one flowmeter; one wet-test meter; one fritted glass filtering crucible, fine; one vacuum desiccator; a source of suction (the water-jet type is adequate).

Potassium hydroxide solution (20 to 30%); monochlorobenzene containing 5 to 10 grams per liter of piperidine; dilute sulfuric acid solution (10% by volume); silver nitrate solution (dissolve 540 grams of silver nitrate crystals in 1 liter of 3.0 N nitric acid with gentle heating and in the cooled solution dissolve such an amount of ferric nitrate crystals as will contain 60.0 grams of anhydrous ferric nitrate).

PROCEDURE

There were set up in series as a gas-scrubbing train the three 25 × 200 mm. scrubbers followed by the two 12 × 150 mm. scrubbers. The first three tubes were charged with reagent solutions to about two thirds their capacity. The potassium hydroxide was placed in the first, the chlorobenzene-piperidine solution in the second, and the 10% sulfuric acid in the third tube. The fourth and fifth (12-mm. tubes) were each charged with approximately 5 ml. of the silver-iron nitrate solution. The gas to be analyzed was passed through the flowmeter, at a rate of about 14 liters (0.5 cubic foot) per hour into the scrubbing train, and then through the wet-test meter, and the temperature and barometric pressure were noted. The flowmeter was used only for convenience in adjusting the gas rate. The silver solution was easily charged into the 0.5-inch test tube (12-mm.) scrubbers by means of a small funnel with the outlet drawn down to a coarse capillary which was inserted in the mouth of the inlet tube.

Sufficient gas sample was passed to yield 100 to 150 mg. of $Ag_2C_2.AgNO_3$, equivalent to about 7 to 10 ml. of pure acetylene or about 0.5 cubic foot of coke-oven gas having a concentration of 0.05% acetylene.

In using the method for gases having a high concentration of acetylene the sample required is so small that a portion of the cleaned gas is measured in a metering tube and dribbled slowly through the two silver nitrate tubes. Figure 1 shows the metering tubes.

Caution. This amount of precipitate was enough to give reasonably accurate results. More than necessary quantities should not be used as $Ag_2C_2.AgNO_3$ is a powerful detonating material. The authors have run many safety tests on $Ag_2C_2.AgNO_3$

and have never been able to detonate it by simple heating below 200° C., which is in accordance with the findings of Taylor and Rinkenbach [9]. But the dry crystals can be readily detonated by a static spark. Percussion of any reasonable intensity apparently will not detonate the dry powder if both anvil and hammer are in electrical equilibrium. Goggles were worn in handling the dry residue and tongs were used for holding the crucible; care was employed to touch the tongs to the surrounding glass to discharge them prior to grasping the crucible and also to touch the handle of the tongs to the balance upright just before placing the crucible on the balance pan. After the analysis was completed the residues were immediately treated with dilute hydrochloric acid to decompose the acetylide. Since these precautions were adopted, not a single detonation of the material has been experienced in many tests run during about two years of work.

After a sufficient gas sample had been scrubbed, the two silver-iron nitrate tubes were removed and the volume of sample taken, temperature, and barometric reading were recorded. A slow current of air was passed through the two silver-iron nitrate tubes for about 10 minutes to remove or minimize traces of metallic silver that may have formed. The contents of the tubes were emptied into a 400-ml. beaker and the tubes were washed thoroughly with distilled water. The solution in the beaker was diluted to about 300 ml. with distilled water added slowly with stirring. The contents were then poured through the previously tared fritted-glass crucible mounted in a suction flask, the walls of the beaker were washed with water, these washings were passed into the crucible, and the beaker was drained. At this point, if any cloudy residue remained on the walls of the 0.5-inch test tubes or on the walls of the 400-ml. beaker, it was removed by rinsing with 2 or 3 ml. of strong silver nitrate solution, which was then diluted in the beaker with thirty times its volume of distilled water and poured through the filter.

The filter was then thoroughly washed with water, the crucible removed, and the outside dried with a clean linen cloth, placed back in the suction flask, and filled twice to the rim with pure acetone. Each increment of acetone was withdrawn by limited suction and the last of the acetone was removed by allowing the crucible to remain on the suction system for about 5 minutes. The crucible was seized in tongs and removed to a vacuum desiccator (containing sulfuric acid) for about 15 to 30 minutes to remove traces of moisture deposited on the walls during evaporation of the acetone. It was then weighed. For most purposes the gain in weight represents, with sufficient accuracy, the acetylene of the sample in the form of $Ag_2C_2.AgNO_3$.

Occasionally gases other than coke-oven gas, very high in hydrogen, will produce more metallic silver than the solution can compensate, giving too high results for acetylene. In such a case, onto the dried and weighed filter residue were poured about 5 ml. of neutral 35% silver nitrate solution, which was let stand a few minutes, and then removed by suction. This procedure was repeated four times, followed by thorough washing with water and finishing with acetone and drying as mentioned. Again the crucible was weighed and the loss in weight represented the true weight of silver acetylide-nitrate obtained by removal of acetylene from the sample.

The effect of olefins in this analysis was also investigated. It was found that the lighter olefins, at least, had no generally adverse effect on the method. Fairly satisfactory results were obtained where known amounts of acetylene were added to pure ethylene and propylene. Very high concentrations of butadiene, however, caused mechanical difficulties. Butadiene gas, when passed through 30% silver nitrate in 3 N nitric acid solution, formed a gummy deposit which interfered with filtration and
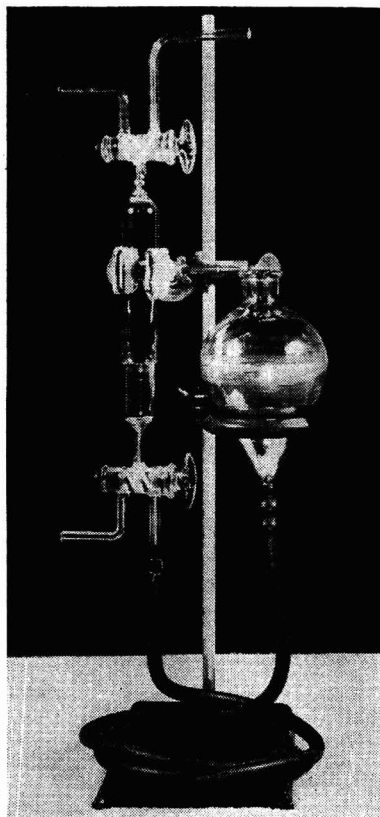

Figure 1.   Gas Metering Tube

weighing. This butadiene contained 0.42% alkyl acetylenes and no simple acetylene (C_2H_2). When passed through neutral 30% silver nitrate, no gummy residue was formed and no precipitate produced upon dilution. The inference is that the gummy residue was due to a polymerization of alkyl acetylene, perhaps with butadiene. Neutral silver nitrate solution, therefore, can be used for determining acetylene in gas of high butadiene concentration. Where appreciable hydrogen is present in the butadiene, neutral silver nitrate leaves something to be desired and search for a better procedure was undertaken. It was found that coke-oven gas could be scrubbed with strong sulfuric acid to remove olefins previous to the silver nitrate scrubbing without affecting the results for acetylene content. Accordingly, butadiene, free of normal acetylene, was diluted with a previously analyzed coke-oven gas to 15 to 20% of butadiene content and in the first instance this gas was scrubbed with 30% neutral silver nitrate to determine the acetylene; and in other instances the gas was passed through fairly concentrated sulfuric acid and then through the acid iron silver nitrate to determine acetylene. The results obtained in both cases were satisfactory, as shown in Tables I and II.

CALCULATION OF RESULTS

$$\frac{\text{Grams of } Ag_2C_2.AgNO_3 \times 0.1905}{\text{cubic feet of gas sample (cor.)}} = \text{vol. } \% \ C_2H_2 \text{ in gas}$$

There is considerable confusion in the literature concerning the density of acetylene. The above calculation was based upon an average value of two densities given by Sameshima [6] and Stahlcross [8]—namely, 1.1747 and 1.1791 grams per liter of acetylene (NTP).

Tables III and IV set forth analytical results obtained by this method upon samples of synthetic acetylene and mixtures. Except as noted, the coke-oven gas used (see especially Table V) was bottled gas stored in steel cylinders at 1000 pounds' pressure, taken from sources representing widely different coke-oven operations. In the authors' experience acetylene content in coke-oven gas tends to increase with oven-top temperature.

Table I.   Effect of Sulfuric Acid Scrubbing on Acetylene Content of Coke-Oven Gas

H_2SO_4, Concentration, %	C_2H_2 in Gas, %	C_2H_2 Found, %
95	0.113	0.110[a]
91	0.113	0.111[a]
87	0.113	0.112[a]

[a] Acid iron silver nitrate scrubbing solution.

Table II.   Analysis of Coke-Oven Gas Plus Added Butadiene

Butadiene, %	H_2SO_4 Concentration, %	C_2H_2 in Gas, %	C_2H_2 Found, %
20	95	0.113[a]	0.114 by direct weight 0.112 by dif. in weight
15	None	0.072[b]	0.070 by direct weight 0.070 by dif. in weight

[a] Acid iron silver nitrate scrubbing solution.
[b] Neutral silver nitrate scrubbing solution.

From Table IV it is apparent that, where hydrogen is present in appreciable quantities, either the acid solution containing ferric nitrate must be employed or, if the neutral silver nitrate is used, the determination must be made by difference—i.e., the original filter residue must be weighed and the silver carbide dissolved in neutral 35% silver nitrate solution to separate it from the metallic silver present, and the crucible washed, dried, and weighed as described.

DISCUSSION OF METHOD

Where there is no hydrogen in the gas to be analyzed, the ferric nitrate may be left out of the scrubbing solution. Its principal role is to inhibit the formation of metallic silver. In fact, a simple 35% aqueous silver nitrate solution may be used if desired.

The potassium hydroxide was employed in the scrubbing train to remove acid gases that will interfere by precipitation or reduction of the silver nitrate. The piperidine reagent removes appreciable amounts of organic sulfur. The acid takes out ammonia and organic bases. If any of these classes of materials are known to be absent, the respective reagent tubes may be omitted.

If acetylene is passed into a solution containing more than about 30% of silver nitrate, the acetylene is retained but initially no precipitate is produced. But upon reaching saturation relatively large rhombohedral crystals are formed that have the formula $Ag_2C_2.6AgNO_3$ (7), and, when dry, detonate only very feebly upon heating (7). Upon treatment with a large amount of water they decompose completely to silver acetylide-nitrate.

For at least two reasons it is not desirable to attempt drying silver acetylide-nitrate at a high temperature: First, because of the explosion hazard; second, because the substance is analytically unstable at increased temperatures. It was found possible by very cautious and somewhat prolonged heating, to decompose the silver acetylide-nitrate sufficiently that upon subsequent

heating to beyond the detonating temperature no explosion took place. Where silver carbide was precipitated and allowed to stand for a day or two in the dilute nitric acid solution before filtration, the analysis showed low results. For these reasons the prescribed drying procedure is recommended.

The directions call for diluting the silver nitrate solution to about 15 grams per liter slowly with stirring to precipitate the silver acetylide. If the total amount of water is added quickly, there is danger that the acetylide will be thrown down in a colloidal form, in which condition a small portion of it will pass and the bulk of it will later seal the filter. If approximately the first eight volumes of water are added slowly with stirring, the silver carbide precipitate will suddenly coagulate. The remainder of the water may then be added quickly and the solution will pass through the filter readily in a clear state.

A convenient method of making small amounts of acetylene for testing purposes is to place a little calcium carbide in a 100-ml. flask and allow a solution of monoethanolamine and water (1 volume of monoethanolamine to 1.5 volumes of water) to drip slowly upon it. The gas is evolved quietly by this procedure and is then scrubbed by passing through a tube charged with 30% potassium hydroxide after having passed through a sulfuric-chromic acid mixture (four volumes of 95% sulfuric acid plus one volume of water, cooled, and saturated with chromic acid). After purging of the train the acetylene is collected in a container over mercury. This gas analyzes better than 99.5% acetylene.

The activity of the strong silver nitrate solution is illustrated by the fact that, where three 12 X 150 mm. test tubes were used in series to scrub coke-oven gas at a rate of 14 liters (0.5 cubic foot) per hour, 98% of the acetylene was found in the first tube, the remainder in the second tube, and none in the third tube, as evidenced by a lack of turbidity upon dilution, which is a very sensitive test. Acetylene present to the extent of only a fraction of a part per million yields a turbidity with very dilute silver nitrate solutions.

Under the conditions of the authors' experimental work hydrogen appears to be the only constituent of coke-oven gas that is capable of reducing silver nitrate to metallic silver. This reduction does definitely take place with hydrogen, though it has been denied in the literature (3). Furthermore, the liberated nitric acid attacks the metallic silver, a portion of the acid reforming silver nitrate and a portion being destroyed by reduction in the well-known manner. This reaction would act adversely upon results in methods where acetylene is determined by shaking the gas with silver nitrate and titrating the liberated acid. The magnitude of the error would probably depend upon the concentration of hydrogen in the gas, the time and vigor of agitation of the sample, and any unscheduled delay in titrating the liberated acid.

Contradictions in the literature concerning the reduction of silver nitrate solutions by hydrogen have presumably arisen because the reduction is rather slow, it depends upon the concentration of hydrogen actually in the solution and hydrogen does not diffuse rapidly into a solution, and the nitric acid formed by the reduction tends to react on the metallic silver produced. For example, if one places a solution containing 300 grams per liter of silver nitrate in 3 N nitric acid in a flask under an atmosphere of hydrogen, if it is shaken perhaps one minute, no metallic silver will be visible, but if it is shaken 15 minutes a distinct crystalline precipitate of metallic silver will appear. Upon standing a few minutes the precipitate will vanish but may be brought back by additional shaking. This cycle can be repeated indefinitely. Nitric oxide is noticeably formed in the process, giving a slight net reduction in gas volume. This phenomenon did not occur when carbon monoxide was substituted for the hydrogen.

The addition of ferric nitrate to the silver nitrate scrubbing solutions lowers somewhat the solubility of the solution for acetylene-silver complexes. If the silver-iron nitrate solution is used for scrubbing, crystals of $Ag_2C_2.6AgNO_3$ will appear in the scrubbing tube before a sufficient sample has been scrubbed to yield 200 mg. of $Ag_2C_2.AgNO_3$. The apparent bulk of this precipitate

Table III. Analysis of Acetylene Prepared Calcium Carbide[a]

Sample No.	Percentage of C_2H_2 Found		Acid Titration
	Direct weight	Dif. in weight	
1	100.03	99.87	
2	99.62	99.58	99.34

[a] Gas scrubbed with chromic-sulfuric acid followed by potassium hydroxide solution and stored over wet mercury.

Table IV. Analysis of Synthetic Mixtures of Acetylene in Gas

Carrying Gas	Percentage of Acetylene Found			Type of Scrubbing Solution
	Added	By direct wt.	By difference	
Nitrogen	0.0511	0.0512	....	Neutral 35% AgNO₃
	0.0838	0.0836	0.0834	a
	0.0763	0.0767	0.0765	a
	0.0568	0.0568	....	a
Hydrogen	0.0838	0.1105	0.0845	Neutral 35% AgNO₃
	0.0763	0.0799	0.0757	a
	0.0838	0.0842	0.0830	a
Ethylene-propylene[b]	0.0877	0.0869	....	a

a See Table V.
b Half and half mixture.

Table V. Analysis of Coke-Oven Gas

Source	Operator No.	Percentage of C_2H_2 Found		Type of Scrubbing Solution
		By direct wt.	By difference	
Cyl. 1	1	0.0724	0.0716	Neutral 35% AgNO₃
	1	0.0720	0.0707	a
Cyl. 2	2	0.0917	0.0736	Neutral 35% AgNO₃
	2	0.0906	0.0731	Neutral 35% AgNO₃
Cyl. 3	2	0.1135	0.1124	a
	2	0.1131	....	a
Plant main	2	0.1041	....	a
	2	0.1076	0.1047	a
	2	0.1164	....	a
	2	0.1107	....	a

a Scrubbing solution: 245 grams of AgNO₃ and 42 grams of Fe(NO₃)₃.9 H₂O dissolved in 455 ml. of 3 N HNO₃.

supplies a rough means of judging the time to discontinue sampling. It seems reasonable that the method could be applied with variations to the determination of acetylene in solution where the solvent does not react with silver nitrate.

All reagents, including the distilled water, must be free of substances, such as chlorides, that are capable of precipitating silver salts from the scrubbing solution.

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Spectrophotometric Estimation of Tryptophan

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The absorption spectrum of the blue color produced in the tryptophan–glyoxylic acid reaction has been found to have three distinct absorption regions, at 2800, 3700, and 5700 Å. Increasing the period of heating during development of the blue color increased intensity at the two lower wave lengths and decreased the intensity of the 5700 Å. band. Tryptophan estimations were carried out on several tryptophan derivatives and proteins at the three wave lengths. Separation of tryptophan from tyrosine and phenylalanine in the protein hydrolyzates, before color development, gave more consistent results at the various wave lengths. The reaction gave high values for apparent tryptophan with unhydrolyzed proteins.

THIS paper is concerned with the estimation of tryptophan by means of the blue color developed by glyoxylic acid in the presence of condensing and oxidizing agents.

Adamkiewicz (3) seems to have been the first to note that when a dilute solution of egg white was added dropwise to concentrated sulfuric acid, a range of colors—green, yellow, orange, red, and finally violet—was produced. He found that if the egg white had been treated previously with glacial acetic acid, only a blue-violet color resulted. Hopkins and Cole (18) showed that the blue color occurred only when the acetic acid was impure, the impurity being glyoxylic acid. Rosenheim (23) demonstrated that the presence of an oxidizing agent was a necessary part of the test. On the other hand, Mottram (21) attributed a failure of the glyoxylic acid test to the presence of an excess of oxidizing agent in the sulfuric acid employed and Breidhal (5) showed that any excess of oxidizing agents could be removed from the acid by suitable reducing agents.

Fearon (11) recognized that the glyoxylic acid reaction might be made a basis for the estimation of tryptophan. He stated that two different colored substances, red and blue respectively, could be formed, depending on the amount of the reactants employed. Several workers (12, 13, 15, 19, 30) have shown that 2,3,4,5-tetrahydro-β-carboline-4-carboxylic acid was easily obtained by the interaction of tryptophan with aldehyde under various conditions. Harvey et al. (14) noted that when the pyrindole compound was brought into contact with sulfuric acid and a trace of oxidizing agent was added, a blue color developed which slowly was transformed to a dirty green and finally a permanent yellow. They pointed out that the first step in the glyoxylic acid reaction probably was formation of the pyrindole compound which later became oxidized to the blue color typical of the reaction. Their attempts to isolate the pigment were unsuccessful.

Winkler (31) developed the glyoxylic acid method for colorimetric comparisons of tryptophan content. Shaw and McFarlane (24) adapted Winkler's method to a photoelectric determination in which the light transmittance was measured at 520 to 540 mμ and the tryptophan estimated from a calibration curve. Lately, Eckert (10) has coupled diazotized tryptophan with N-(1-naphthyl)ethylenediamine to give a red color which is adaptable to the photoelectric technique.

In recent years several investigators have employed the glyoxylic acid method, principally as used by Shaw and McFarlane. Sullmann (26) in an investigation of tryptophan derivatives found that L-tryptophan gave less color intensity than several of its derivatives. In view of the author's results, it seems likely that Sullmann's original tryptophan was impure and that the derivatives were considerably purer. He reported 83.6% recovery of tryptophan purposely added to proteins hydrolyzed by 10% sodium hydroxide. This compares well with the value of 81% recovery (7) reported some years ago, which has been duplicated in

other laboratories. Sullmann was the first to report that some proteins do not require hydrolysis but only solution in sodium hydroxide to give the glyoxylic acid reaction. Ciocalteu and Isacescu (8) reported that preliminary hydrolysis of the protein was essential but that the glyoxylic acid reaction did not take place in the presence of oxidants or trichloroacetic acid. The author has been unable to confirm the two latter statements. Hauschildt, Isaacs, and Wallace (16) have compared the glyoxylic acid method, the N-(1-naphthyl) ethylenediamine method, and the microbiological method of McMahon and Snell (20) and reported that the latter gave the highest results for tryptophan. They also confirmed Sullmann's observation that preliminary hydrolysis of protein was not necessary.

PREPARATION OF MATERIALS

L-Tryptophan was a sample from Hoffmann-La Roche and was recrystallized twice from butyl alcohol; melting point 273° (corrected, decomposed). Nitrogen content was determined by the method of Campbell and Hanna (6). Found 13.68%; calculated 13.72%.

Glycyl-L-tryptophan was prepared from the above sample of L-tryptophan by the method of Abderhalden and Kempe (1); melting point 302° (corrected).

Acetyl-L-tryptophan was prepared from the above sample of L-tryptophan by the method of du Vigneaud and Sealock (9); melting point 189–190° (corrected).

L-Tryptophan methyl ester was prepared from the above L-tryptophan by the method of Abderhalden and Kempe (2); melting point 89.5° (corrected). The hydrochloride had a melting point of 214° (corrected, decomposed).

L-Tyrosine was purified from a large commercial lot employing hydrochloric acid and ammonium acetate (25) and finally recrystallized four times from hot water; melting point 307° (corrected). $[\alpha]_D^{20}$ 11.8° (C = 5.00% in 4% hydrochloric acid).

L-Phenylalanine was a commercial preparation recrystallized twice from hot water; melting point 285° (corrected, decomposed). Neither the L-tyrosine or L-phenylalanine gave the blue color of the glyoxylic acid reaction and, hence, they were free from tryptophan.

Casein was a sample of crude casein prepared by a modification of the acid-precipitation method of Van Slyke and Baker (29).

Edestin was prepared from hemp seed by the method of Osborne (22).

Zein was prepared by Swallen's method (28).

Insulin was from a sample of crystalline zinc salt of insulin kindly furnished by Eli Lilly and Company.

Glyoxylic acid solution was prepared by Benedict's method (4).

The moisture content of the foregoing preparations (except glyoxylic acid) was determined in an evacuated Abderhalden dryer (0.1 mm. and 61°) and all weights and concentrations employed were calculated to a dry basis.
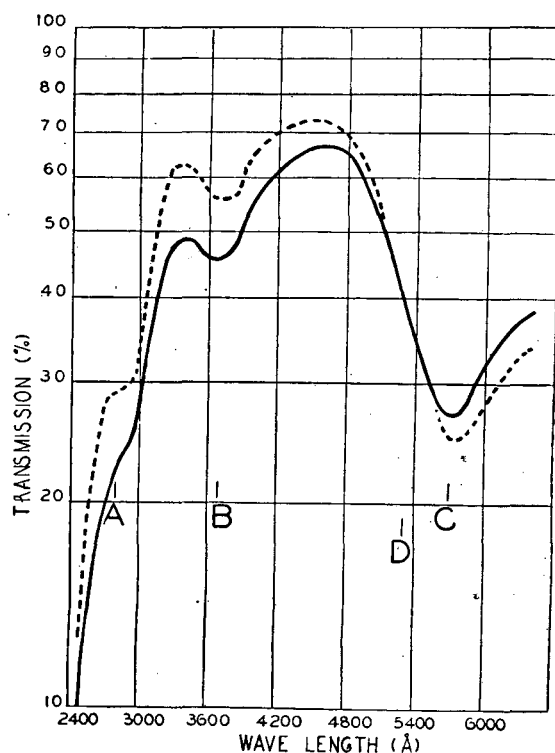
Figure 1.   Transmittance Curve for Blue Color in Tryptophan–Glyoxylic Acid Reaction

Broken line, heating for 5 minutes at 100°
Solid line, heating for 20 minutes at 100°

ABSORPTION SPECTRUM OF BLUE COLOR

Shaw and McFarlane (24) examined the spectrum of the blue color obtained in the tryptophan–glyoxylic acid reaction, in the region 4500 to 6500 Å., and found an absorption band with a maximum in the vicinity of 5500 Å., the wave length which they employed for photoelectric measurements in their method. The author examined the spectrum of the blue color over the entire range 2400 to 6400 Å., and found three regions of absorption (low transmittance) with maxima at 2800, 3700, and 5700 Å. It was found that, in developing the blue color, the period of heating at 100° shifted the intensity of the bands considerably. With longer heating the intensity of the bands at 2800 and 3700 Å. increased while the band at 5700 Å. decreased. This would indicate transformation of one absorbing substance into another by the influence of heat.

In Figure 1 are shown the transmittance curves obtained with 5 minutes' heating at 100° (dotted line) and with 20 minutes' heating (solid line) in developing the blue color. In the region of 5400 Å., where Shaw and McFarlane made their measurements, additional heating beyond 5 minutes makes no change in the absorption, as these authors note. In his work the author has employed a 20-minute heating period for developing the color in all tryptophan estimations. The curves in Figure 1 contained identical amounts of tryptophan and reagents and differed only in period of time heated to develop the color. The content of tryptophan in the blue solutions represented by the curves in Figure 1 was 1 × 10⁻⁴ mole per liter. The transmittance was measured in a Beckman quartz spectrophotometer against a blank containing identical amounts of reagents but from which tryptophan was omitted.

Calibration curves were prepared relating tryptophan content and transmittance at wave lengths 2800, 3700, and 5700 Å. (Figure 1, A, B, C, D, represent wave length used by Shaw and McFarlane). The calibration curves were straight lines, as would be expected from Beer's law; from the transmittance reading the tryptophan content was read off directly. The blue color faded about 3% in intensity in 24 hours; consequently readings should be made within 2 or 3 hours after development of the color.

METHOD

The method employed in developing the blue color was essentially that of Winkler.

To a 10-ml. flask 0.2 to 1.5 ml. of a 0.0005 M aqueous solution containing tryptophan, 0.2 ml. of a 0.004 M aqueous glyoxylic acid solution, and 0.3 ml. of 0.01 M copper sulfate solution were added and the mixture was diluted to 3.0 ml. The solution was cooled in an ice bath, while 5.0 ml. of concentrated sulfuric acid were added dropwise, and the mixture was shaken constantly. The flask was allowed to come to room temperature and after standing 20 to 30 minutes, the blue color was developed by immersion of the flask in a bath of boiling water for 20 minutes. A blank containing the reagents, but no tryptophan, was prepared and heated at the same time for the same period. After cooling, the volume was made up to 10 ml. with 3 to 5 sulfuric acid (to avoid heat evolution) and after thorough mixing, the sample and blank were transferred to 1 × 1 × 4.7 cm. quartz observation cells, the spectrophotometer was adjusted on the blank for the wave length employed (2800, 3700, and 5700 Å.), and the light transmittance of the unknown was read on the instrument. Reference was made to the calibration curves for converting transmittance directly to tryptophan concentration.

RESULTS

In Table I are given results obtained with tryptophan and several of its derivatives. These show that tryptophan may be determined with excellent accuracy over a range of concentration when there are no interfering substances present. The results are equally good at the three wave lengths employed.

Interfering Substances. To employ the above method on hydrolyzates or mixtures containing tryptophan, tyrosine, and phenylalanine, note must be made that the latter amino acids have absorption bands at 2750 Å. (17) and may be expected to interfere with the accuracy of tryptophan estimations in that vicinity.

In determining the extent of this interference, the data in Table II were collected. The transmittance values of the various mixtures in Table II are given after development of the blue color and may be compared directly without conversion to apparent tryptophan content. Blanks with no added tryptophan were made for

Table I.   Estimation of Tryptophan in Derivatives

Compound	M.W.	Trypto-phan	λ = 2800 Å.		λ = 3700 Å.		λ = 5700 Å.	
			Trypto-phan found, mg.	Re-covery, %	Trypto-phan found, mg.	Re-covery, %	Trypto-phan found, mg.	Re-covery %
L-Tryptophan	204.2	0.050	0.0491	98.2	0.0492	98.4	0.0480	96.0
		0.100	0.0985	98.5	0.0987	98.7	0.0972	97.2
		0.150	0.1485	99.0	0.1488	99.2	0.1480	98.6
		0.200	0.1988	99.4	0.1990	99.5	0.1982	99.1
		0.250	0.2488	99.5	0.2494	99.8	0.2480	99.2
Glycyl-L-trypto-phan	261.2	0.050	0.0482	96.4	0.0490	98.0	0.0480	96.0
		0.100	0.0987	98.7	0.0988	98.8	0.0982	98.2
		0.150	0.1482	98.8	0.1488	99.2	0.1477	98.5
		0.200	0.1992	99.6	0.1993	99.7	0.1978	98.9
		0.250	0.2490	99.6	0.2496	99.9	0.2475	99.0
Acetyl-L-trypto-phan	246.2	0.050	0.0487	97.4	0.0489	97.8	0.0484	96.8
		0.100	0.0982	98.2	0.0986	98.6	0.0988	98.8
		0.150	0.1486	99.1	0.1490	99.3	0.1492	99.5
		0.200	0.1995	99.0	0.1996	99.8	0.1994	99.7
		0.250	0.2495	99.8	0.2498	99.9	0.2498	99.9
L-Tryptophan methyl ester	218.2	0.050	0.0488	97.6	0.0492	98.4	0.0490	98.0
		0.100	0.0996	99.6	0.0994	99.4	0.0992	99.2
		0.150	0.1494	99.6	0.1496	99.7	0.1490	99.3
		0.200	0.1994	99.7	0.1995	99.8	0.1990	99.5
		0.250	0.2500	100.0	0.2500	100.0	0.2496	99.8

each mixture. A lower transmittance value than for tryptophan alone means light absorption due to the presence of tyrosine or phenylalanine and consequently a high apparent tryptophan value. In general, the error due to equal molar quantities of tyrosine was greater than that of phenylalanine. At 2800 Å. tyrosine lowered the apparent tryptophan content 3 to 6%, while phenylalanine increased it 4 to 6%, depending on the concentration. At 3700 Å. both tyrosine and phenylalanine lowered the apparent tryptophan content around 5%. At 5700 Å. both tyrosine and phenylalanine increased the apparent tryptophan content, the former being more effective. From this it would appear that for precise work on mixtures containing tryptophan, a preliminary separation from tyrosine and phenylalanine was essential.

Applying the tryptophan-glyoxylic acid reaction to the analysis of proteins, the author has used casein, edestin, zein, and insulin. These have been employed after hydrolysis with 20% sodium hydroxide, with no hydrolysis (the protein simply being dissolved in the same solvent), and also after separation of tryptophan as its mercury salt from the hydrolyzed proteins. On account of the brown color of the hydrolyzate, readings of light transmittance were impossible at 2800 Å. Decoloration by charcoal or other adsorbents was impossible on account of the simultaneous removal of tryptophan. The author's results are recorded in Table III, together with those of other investigators that have employed the Shaw and McFarlane method.

Results have been similar to those of other workers in showing higher apparent tryptophan values (3 to 5% higher) on unhydrolyzed proteins than on hydrolyzed proteins, even though the latter values contain a recovery factor. Neither zein or insulin showed any trace of blue color in the glyoxylic acid reaction and therefore contain no tryptophan.

Separation of tryptophan from the hydrolyzed proteins by precipitation as its mercury salt (7), and thus removing the interference of tyrosine and phenylalanine, gave results that agreed well among themselves for all three wave lengths. However, the average was practically the same as where the mercury separation was not employed on the hydrolyzate. These results were definitely not so high, however, as the more consistent values from the unhydrolyzed samples. The data at 2800 Å. are the least consistent for the unhydrolyzed proteins, but the average for the three wave lengths for a given protein is almost identical with the determinations on hydrolyzed materials.

The author introduced the idea of the correction factor for tryptophan recovery some years ago (7) in analyses of casein samples which had been used in molecular weight determinations in Svedberg's ultracentrifuge (27). It was well known that hydrolysis of proteins by acid completely ruined any tryptophan present and that only by hydrolysis with alkali or enzymes could tryptophan be recovered at all. In estimating the amount of recovery of tryptophan from the alkali digestion, known amounts of tryptophan were added to the protein before hydrolysis, and the total tryptophan (from protein plus added tryptophan) in the hydrolyzate was estimated by bromination, after tryptophan had been separated from other amino acids by the mercury precipitation. This gave a series of digests containing $X + A$, $X + 2A$, $X + 3A$, etc., amounts of tryptophan, respectively (where X equals the tryptophan present in the protein and A represents the tryptophan purposely added before hydrolysis), from which the recovery factor of A was evaluated. It was assumed that the same recovery factor applied to X (tryptophan liberated from the protein) and the latter was corrected accordingly. This was as close an estimate of the tryptophan content of a protein as one could make.

Present results with unhydrolyzed proteins indicate an even higher tryptophan content. In terms of tryptophan recovery this would indicate actually a smaller tryptophan recovery from the protein part of the alkali digest than that found for added tryptophan. This is perhaps possible and would indicate that perhaps one is not justified in applying the experimentally found recovery factor for tryptophan itself to its recovery from a protein.

Table II. Transmittance of Mixtures of Tryptophan, Tyrosine, and Phenylalanine

Molar Ratios[a]			% Transmittance		
Trypto-phan	Tyrosine	Phenyl-alanine	2800 Å.	3700 Å.	5700 Å.
1	0	0	22.8	45.7	27.0
1	1	0	23.9	47.8	26.8
1	2	0	25.3	48.1	24.3
1	0	1	21.4	48.0	26.8
1	0	2	21.1	47.8	26.1
1	1	1	22.8	48.1	26.7
1	2	2	24.6	48.8	24.4

[a] 0.0001 Mole of tryptophan present throughout except in blanks.

Table III. Tryptophan Content of Proteins

	Hydrolyzed by 20% NaOH Soln. (Corrected for 81% Recovery)			Hydrolyzed by 10% NaOH or Satd. Ba(OH)₂ (Shaw and McFarlane Method)	
	2800 Å.	3700 Å.	5700 Å.	NaOH	Ba(OH)₂
Casein		1.36	1.38	1.04 (24) 1.25[a] 1.41-1.46[b]	1.25 (24) 1.50[a]
Edestin		1.42	1.47	1.28[a]	1.38[a]

Hydrolyzed by 20% NaOH Soln. Tryptophan Separated as Hg Salt (Corrected for 81% Recovery)

| Casein | 1.36 | 1.40 | 1.36 |
| Edestin | 1.42 | 1.45 | 1.44 |

Unhydrolyzed, Dissolved in 20% NaOH Soln.

	2800 Å.	3700 Å.	5700 Å.		
Casein	1.32	1.41	1.42	1.25 (24) 1.38[a] 1.35-1.46[b]	
Edestin	1.30	1.50	1.54	1.35-1.46[a]	
Zein	(0.04)	0	0		
Insulin	(0.06)	0	0		

Casein (M.W. 98,000 fraction) gave 1.24% tryptophan (corrected) by bromate titration (7).

[a] Author reports 83.6 to 84.6% recovery of tryptophan added before hydrolysis (26).
[b] Authors report that tryptophan content was the same whether protein as hydrolyzed under pressure by 20% NaOH or only dissolved in 20% NaOH solution (16).

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Rapid Estimation of Citrus Peel Oil

A New Turbidimetric Method

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A rapid determination of citrus oils is needed for control purposes; the official method in use is 90 minutes long. A rapid procedure is described for the colorimetric estimation of oils in raw and processed citrus juices. The oil is distilled with acetone and steam to a known volume, an aliquot is diluted, and turbidity is determined. A standardization procedure makes possible correlation of results in terms of the official method of the United States Department of Agriculture.

IN THE production of canned citrus juices considerable quantities of peel oil are incorporated by high-speed mechanical extractors, although modern processing plants have several methods of controlling the peel oil content of juices. These plants operate at such high rates that a rapid estimation of the peel oil is necessary for control purposes. In 1941, Scott (*2*) presented a steam-distillation method for determining the amount of peel oil in citrus juices and proposed that the quantity of this oil be used as a measure of undesirable constituents incorporated by the extractors.

Small amounts of essential peel oil are desirable, in that they add materially to both aroma and flavor. Between 0.002 and 0.005% recoverable oil appears to be best for grapefruit juice, and somewhat higher concentrations for orange juice. Higher concentrations of oil are objectionable even in fresh juices and deteriorate in stored juices, as evidenced by the development of turpentinelike flavors. The Production and Marketing Administration, Department of Agriculture as well as industry in general, uses a modified Clevenger method (*3*) for grading purposes. This requires a large sample and about 90 minutes for a single determination. This is far too slow for control work, as modern processing plants are able to handle well over 100 tons of fruit before a single determination can be completed. Recently, Burdick and Scott (*1*) developed a turbidimetric method for the rapid estimation of peel oil. This method involved a simple distillation of juice with ethanol and was found very satisfactory in the research laboratory. However, the denatured ethanols necessitated in
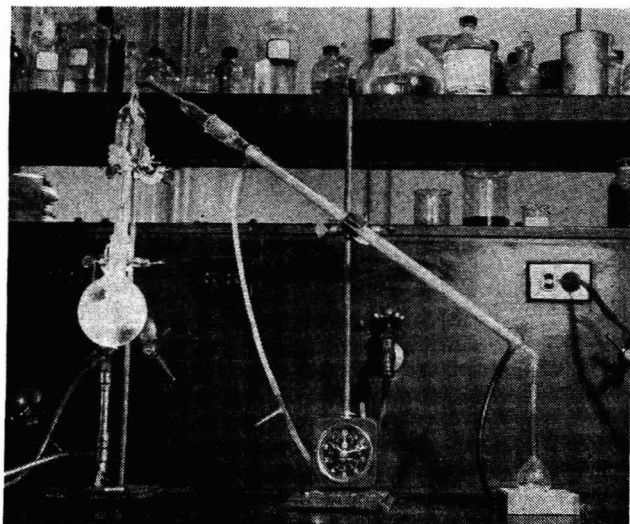
Figure 1. Distillation Apparatus

control laboratories were unsatisfactory, as they produced turbid solutions in all cases upon dilution with water. Subsequent investigations using methanol, butanol, 2-propanol, and mixtures of these alcohols showed them to be either too sensitive or not sensitive enough to variations in peel oil concentrations.

This paper presents a rapid method for the estimation of peel oil, suitable for quantity control in the industrial production of canned citrus juices. Acetone is a satisfactory substitute for ethanol, making available to industrial laboratories a rapid turbidimetric method. It is possible to eliminate the salting-out agent, inasmuch as the acetone-oil distillate attains maximum turbidity within 1 minute upon dilution with water and remains stable at least 5 minutes.

PRELIMINARY EXPERIMENTS

Turbidity measurements on solutions obtained by diluting methanol, butanol, 2-propanol, and acetone solutions containing known concentrations of peel oil indicated the superiority of acetone. By using acetone and peel oil in the concentration range desired (equivalent to 0.000 to 0.050% recoverable peel oil), a practical conformity with Beer's law was obtained.

APPARATUS AND MATERIALS

The distillation apparatus shown in Figure 1 consists of a 500-ml. distilling flask, a standard Kjeldahl distilling trap, and condenser (preferably West type), having its delivery end tapered to fit well down into the neck of a 50-ml. volumetric flask, which serves as the distillate collector. All joints are 24/40 glass ground standard taper. The trap is not entirely necessary, but has proved advantageous when foaming samples are encountered. Turbidimetric measurements were made with a model 400 G Lumetron photoelectric colorimeter, using the blue (420) filter to obtain maximum sensitivity. Acetone meeting A.C.S. or U.S.P. grades is satisfactory, the only requirement being that no turbidity is produced when it is diluted with water.

PROCEDURE

Transfer 100 ml. of a well mixed juice sample by a fast flowing pipet into a 500-ml. distilling flask, then add 25 ml. of acetone. Fit the flask to the distillation apparatus and begin the distillation by rapidly bringing the temperature up to the boiling point with an open flame. Once the mixture is boiling, adjust the rate of distillation so that no vapor is lost. The temperature and amount of cooling water passing through the condenser limit the rate of distillation. Collect exactly 50 ml. of distillate (if the distillate is not clear, use a smaller sample). After agitating to mix the clear distillate, transfer a 5-ml. aliquot to a clean dry colorimetric test tube and add 10 ml. of distilled water. Shake the test tube hard enough to ensure adequate mixing, yet not hard enough to trap tiny air bubbles in the resulting turbid solution.

Prepare a blank for adjusting the photoelectric colorimeter to zero optical density or 100% transmittance by distilling a mixture of 100 ml. of water and 25 ml. of acetone, collecting 50 ml. of distillate, and diluting 5 ml. of distillate with 10 ml. of distilled water. Adjust the colorimeter to zero optical density or 100% transmittance when using this blank and the blue (420) filter. Note the air blank obtained upon removal of the real blank, which

can then be used for future adjustments. Optical density or per cent transmittance measurements should be made within 2 minutes after preparation of the turbid solutions; however, the clear distillates remain stable for several days if kept tightly stoppered. Calculate the per cent recoverable oil by multiplying the optical density reading of the unknown sample by a factor determined experimentally, as explained in the standardization procedure.

STANDARDIZATION AGAINST MODIFIED CLEVENGER METHOD

By preparing a series of solutions containing known amounts of various citrus oils, diluting these with distilled water to make turbid solutions of known oil content, measuring the optical densities of these turbid solutions, and finally plotting the optical densities against the oil concentrations, it is possible to show a slight variation or deviation from Beer's law. However, it is seen from Figure 2 that a straight line results over a considerable concentration range. This straight line does not go through the origin, probably because of the very slight solubility of peel oil in the dilute acetone, which partially explains the nonconformity with Beer's law.
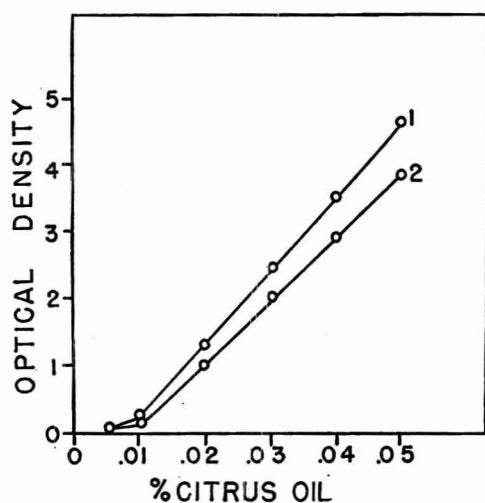
Figure 2. Optical Densities of Turbid Citrus Oil Emulsions

1. Synthetic mix (steam-distilled citrus oil used)
2. Distillate

Discrepancies between the turbidities produced by known concentrations of citrus oils and those found by the modified Clevenger method have been observed—neither the modified Clevenger nor the acetone distillation method recovers 100% of added peel oil. It is thus necessary to establish experimentally the relation between the turbidity obtained by the acetone turbidimetric method and the amount of recoverable peel oil as determined by the modified Clevenger method. This is readily done by making duplicate analyses by both the turbidimetric method and the modified Clevenger method on a series of juice samples containing varying amounts of recoverable oil. Table I shows the results of such a set of duplicate analyses by two analysts. The optical densities are proportional to the oil found by the Clevenger method. The proportionality factor, 0.0906, is calculated from the averages. Thus it is possible to multiply the optical density by the factor 0.0906 to get the per cent recoverable oil that would have been found by the modified Clevenger method. Because the method is empirical, each analyst should standardize his equipment against the modified Clevenger method.

EXPERIMENTAL

The relation between optical density and per cent peel oil is shown in Figure 2.

Curve I was obtained from "synthetic distillates" designed to represent distillates that would be produced by the complete re-

Table I. Comparison of Results Obtained by Modified Clevenger Method with Acetone Distillation Turbidimetric Method

% Recoverable Oil, Clevenger			Optical Density (OD × 10)			% Recoverable Oil, Turbidimetric (OD × 0.0906)	Deviation
1st	2nd	Av.	1st	2nd	Av.		
0.0010	0.0012	0.0011	0.20	0.05	0.13	0.0012	+0.0001
0.0020	0.0010	0.0015	0.20	0.15	0.18	0.0016	+0.0001
0.0010	0.0025	0.0018	0.15	0.10	0.13	0.0012	−0.0006
0.0025	0.0020	0.0023	0.25	0.15	0.20	0.0018	−0.0005
0.0020	0.0025	0.0023	0.25	0.25	0.25	0.0023	0.0000
0.0025	0.0025	0.0025	0.20	0.15	0.18	0.0016	−0.0009
0.0025	0.0030	0.0028	0.20	0.20	0.20	0.0018	−0.0010
0.0080	0.0100	0.0090	0.85	0.80	0.83	0.0075	−0.0015
0.0110	0.0100	0.0105	1.25	1.20	1.23	0.0111	+0.0006
0.0125	0.0135	0.0130	1.60	1.75	1.68	0.0152	+0.0022
0.0140	0.0140	0.0140	1.40	1.45	1.43	0.0130	−0.0010
0.0160	0.0150	0.0155	2.00	1.80	1.90	0.0172	+0.0017
0.0150	0.0165	0.0158	1.80	1.80	1.80	0.0163	+0.0005
0.0175	0.0175	0.0175	1.55	1.65	1.60	0.0145	−0.0030
0.0175	0.0200	0.0188	2.30	2.25	2.28	0.0207	+0.0019
0.0190	0.0200	0.0195	2.25	2.20	2.23	0.0202	+0.0007
0.0210	0.0220	0.0215	2.10	2.20	2.15	0.0195	−0.0020
0.0270	0.0280	0.0275	3.20	3.20	3.20	0.0290	+0.0015
Total		0.1959			21.60		

Table II. Effect of Dilution on Turbidity

Distillate, Ml.	Water, Ml.	Optical Density × 10	% Concn. of Oil	Optical Density per Unit Concn.
5	1	0.03	0.033	0.9
5	2	0.50	0.029	17.3
5	3	0.70	0.025	28.0
5	4	0.90	0.022	40.8
5	5	1.10	0.020	55.0
5	6	1.10	0.018	61.1
5	7	1.10	0.017	64.7
5	8	1.00	0.015	66.7
5	9	0.90	0.014	64.3
5	10	0.85	0.013	65.4

covery of various amounts of peel oil from 100-ml. samples of juice, by dissolving 1 ml. of distilled grapefruit oil in enough acetone to make 100 ml. Aliquots containing 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ml. of this solution were then mixed with enough acetone to make a total of 25 ml. of acetone solution and made up to 50 ml. with distilled water. These samples correspond to distillates from the complete recovery of oil from 100-ml. samples of juice containing 0.005, 0.010, 0.020, 0.030, 0.040, and 0.050% oil. The optical densities of turbid solutions made by mixing 10 ml. of distilled water with 5-ml. aliquots of the above 50-ml. samples were then measured in the photoelectric colorimeter, using the blue filter. A blank containing the appropriate amounts of acetone and water was used to adjust the colorimeter to zero optical density.

Curve 2 was obtained by distilling 100-ml. samples of water with 25 ml. of acetone and 0.005, 0.010, 0.020, 0.030, 0.040, and 0.050 ml. of distilled grapefruit oil, collecting 50 ml. of distillate from each, diluting 5 ml. of these distillates with 10 ml. of distilled water, and measuring the optical densities of the resulting turbid solutions.

It is readily seen from these results that only a proportional amount of oil is distilled. This is also true for other steam-distillation methods. Scott (1) recovered only 77% of added peel oil, whereas these results show a recovery of about 83%. The results given are typical of those obtained with distilled orange oils, distilled lemon oils, cold pressed orange and grapefruit oils, and d-limonene.

Effect of Dilution on Turbidity. To check the effect of dilution on the turbidity, a "synthetic distillate" was made by adding

Table III. Effect of Wave Length on Absorption

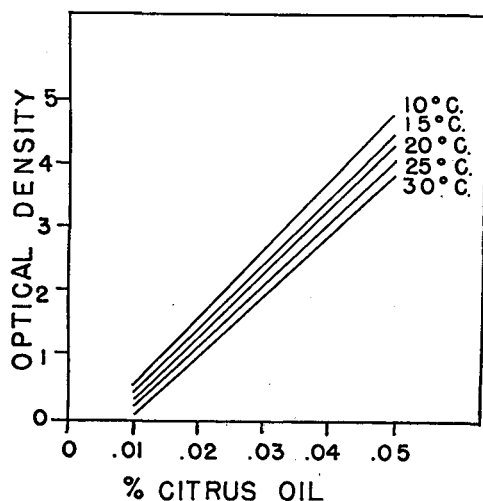| Filter	Wave Length	Optical Density × 10
Violet	370	1.65
Blue	420	2.90
Blue-green	490	1.60
Yellow-green	530	1.45
Orange	580	1.15
Red	650	0.95

Figure 3. Effect of Temperature on Optical Densities of Citrus Oil, Acetone, and Water Emulsions

0.040 ml. of distilled grapefruit oil to 50 ml. of acetone and making up to 100 ml. with water. Turbid solutions were then made by diluting 5-ml. aliquots of this synthetic distillate with various amounts of water. Table II shows the optical densities of these turbid solutions, the per cent concentration of oil, and the optical densities per unit concentration. These results indicate that a maximum optical density was reached when only 5 ml. of water were used to dilute 5 ml. of distillate, but to ensure near maximum turbidity per unit concentration of oil it is advisable to use 10 ml. of water as diluent. By adequate dilution it is possible to obtain all readings in a zone of near constant optical density per unit concentration.

Effect of Wave Length on Absorption. The blue (420) filter, as would be expected, gave the highest absorption. Table III shows the effect of various filters on the optical density of a typical acetone-oil-water emulsion.

Effect of Temperature on Turbidity. To determine the effect of temperature on the turbidity produced when the distillates are diluted with water, a series of acetone-oil-water solutions containing known amounts of oil was distilled and the distillates were collected. Before dilution with water the distillates were brought to the desired temperature in a constant-temperature bath, then diluted with water having the same temperature. Much difficulty was encountered in making the optical density measurements at the low temperatures because of condensation on the colorimetric test tubes. The results of the optical density measurements are shown in Figure 3. Here again, the solubility of citrus oil in the acetone-water solution appears to be the controlling factor. As expected, an increase in temperature causes a decrease in optical density. Slight variations due to temperature are insufficient to necessitate correction for routine analyses.

SUMMARY

A rapid method for the estimation of peel oil in citrus juices, based on distillation of the sample with acetone, gives consistent and reproducible results comparable to those obtained with the time-consuming modified Clevenger method. Complete determinations can be made in about 7 minutes on a sample of only 100 ml.

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Polarographic and Amperometric Determination of Barium

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The polarographic waves of barium in lithium chloride, calcium chloride, and magnesium chloride were studied. Calcium chloride was found to be the best supporting electrolyte for the measurement of the diffusion current of the barium ion, no maximum in the wave being observed in the presence of calcium. With magnesium chloride, diffusion currents were high and a special correction was necessary. The amperometric titration of 0.001 M barium with chromate cannot be carried out conveniently in aqueous medium. In 20, 30, and 50% ethanol the titration can be carried out rapidly with an accuracy of the order of 3%.

POLAROGRAPHIC studies on barium were first made by Heyrovský and Berezicky (1), who found a well defined wave with a pronounced maximum in 0.1 N lithium chloride. The amperometric determination of barium with sulfate was also performed, but poor accuracy was found.

The polarographic behavior of barium in aqueous and ethanol-water mixtures using tetraethylammonium iodide as supporting electrolyte was studied by Zlotowski and Kolthoff (6). The half-wave potential in water vs. the saturated calomel electrode was found to be −1.94 volts, and the waves satisfied the Ilkovič equation.

POLAROGRAPHIC WAVES OF BARIUM IN LITHIUM, CALCIUM, AND MAGNESIUM CHLORIDES

The current-voltage curves were measured with a manual apparatus. The conventional H-shaped cell was used and all

cathode potentials were measured against the saturated calomel electrode. The experiments were carried out in a thermostat at 25° C. Analytical reagent chemicals were used throughout and the ethanol was redistilled.

The capillary, unless otherwise specified, had an initial drop time of 3.6 seconds in 0.1 N lithuim chloride with a disconnected electric circuit. The weight of mercury flowing from the capillary per second under these conditions was 1.002 mg. per second. The height of the mercury column was 20 cm.

Current-voltage curves of barium in 0.1 M lithium chloride show a pronounced maximum which cannot be suppressed by thymol, methyl red, methylene blue, or gelatin. These maxima extend over but a limited voltage range. Although no distinct diffusion current region is observed (see Figure 1) the diffusion current (corrected for the residual current) measured at the minimum was found to be proportional to the concentration as shown in Table I.
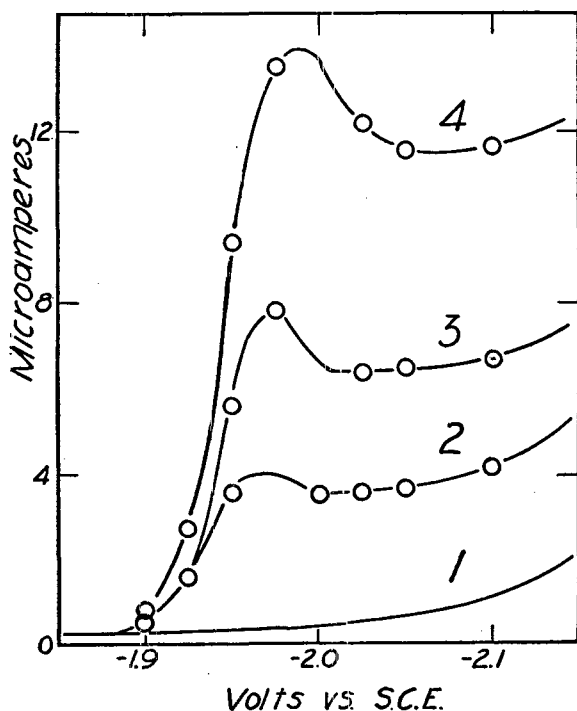
Figure 1.   Polarograms of Barium Chloride in 0.1 M Lithium Chloride

1. Residual current
2. 0.50 × 10⁻³ M barium
3. 1.00 × 10⁻³ M barium
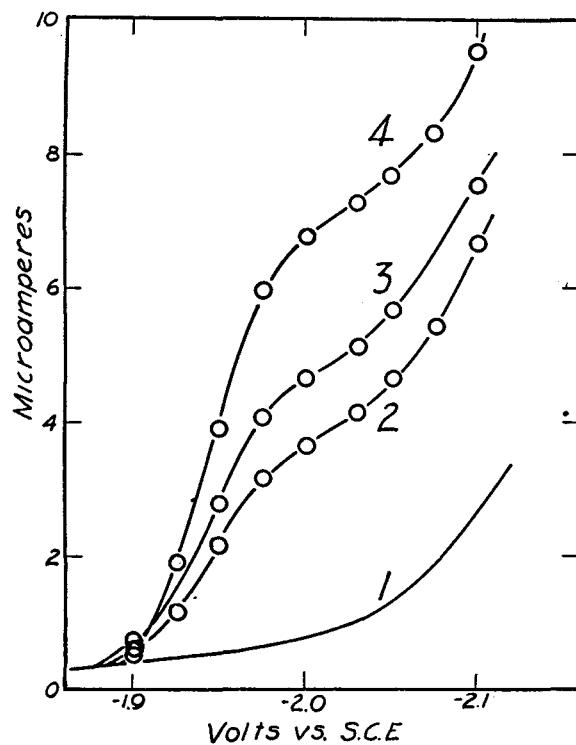4. 1.82 × 10⁻³ M barium

Uncorrected for residual current

Figure 2.   Polarograms of Barium Chloride in 0.05 M Calcium Chloride

1. Residual current
2. 0.48 × 10⁻³ M barium
3. 1.00 × 10⁻³ M barium
4. 1.31 × 10⁻³ M barium

Uncorrected for residual current
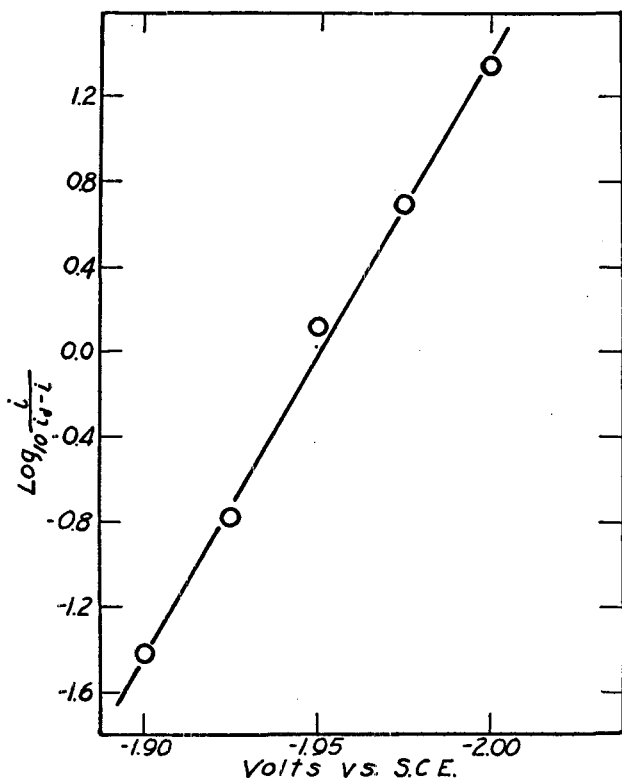
Figure 3.   Analysis of Barium Wave in 0.05 M Calcium Chloride

Log₁₀ (i/i_d − i) plotted against applied potential.   Experimental slope is 0.028
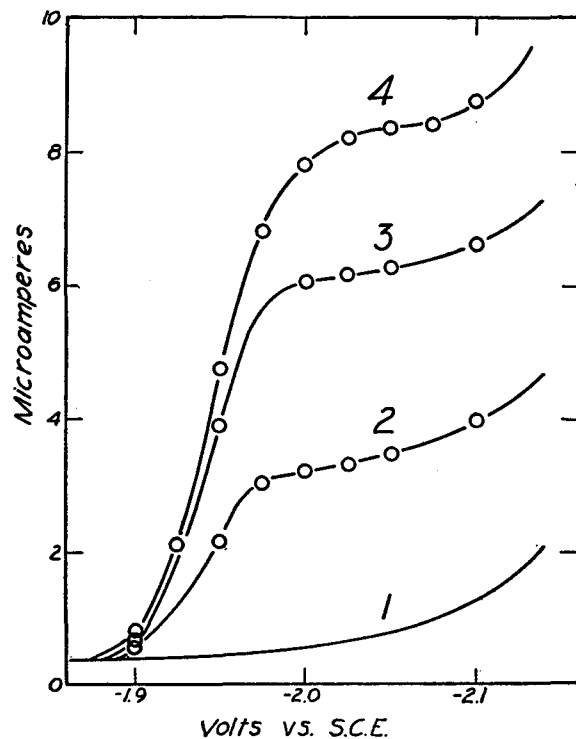
Figure 4.   Polarograms of Barium Chloride in 0.05 M Magnesium Chloride

1. Residual current
2. 0.39 × 10⁻³ M barium
3. 0.57 × 10⁻³ M barium
4. 0.91 × 10⁻³ M barium

Uncorrected for residual current

Table I. Diffusion Current Constant of Barium Measured at $\pi = -2.05$ Volts

0.1 M LiCl			0.05 M CaCl$_2$			0.05 M MgCl$_2$		
C	i_d	i_d/C	C	i_d	i_d/C	C	i_d	i_d/C
$M \times$		$\mu a./M$	$M \times$		$\mu a./M$	$M \times$		$\mu a./M$
10^3	$\mu a.$	$\times 10^3$	10^3	$\mu a.$	$\times 10^3$	10^3	$\mu a.$	$\times 10^3$
0.50	2.90	5.80	0.48	2.72	5.70	0.39	3.33	8.65
1.00	5.67	5.67	1.00	5.55	5.55	0.57	4.38	7.71
1.82	10.76	5.91	1.31	7.60	5.80	0.91	6.38	7.01

In 0.05 M calcium chloride, the current-voltage curves of barium are smooth and S-shaped and do not show any maximum. These curves are given in Figure 2 and the proportionality of i_d to C is included in Table I. An analysis of the 1.31×10^{-3} M barium chloride wave, obtained by plotting $\log \dfrac{i}{i_d - i}$ against the cathode potential, yields a straight line with a slope of 0.028 (Figure 3). The Heyrovský-Ilković equation predicts a slope of 0.029 at 25° C. for a reversible reduction.

The diffusion current of barium in 0.05 M calcium chloride was calculated using the Ilkovic equation. The capillary used in this determination had values of $m = 0.704$ mg. sec.$^{-1}$ and $t = 2.87$ sec. at $E = -2.08$ volts. The concentration of barium was 5.00×10^{-4} M. The calculated value of i_d is 1.67 microamperes and the experimental diffusion current was also 1.67 microamperes.

The current-voltage curves of barium in 0.05 M magnesium chloride do not give a maximum, but no distinct diffusion current region is observed. The apparent diffusion currents are abnormally large. The magnesium ion itself produces abnormally high currents; this is attributed to the catalysis of the discharge of hydronium ions by traces of magnesium in the amalgam (7). In Figure 4 barium waves in 0.05 M magnesium chloride are shown. If the currents observed with magnesium chloride as supporting electrolyte are corrected for the residual current, the diffusion current of barium is still too large and the diffusion
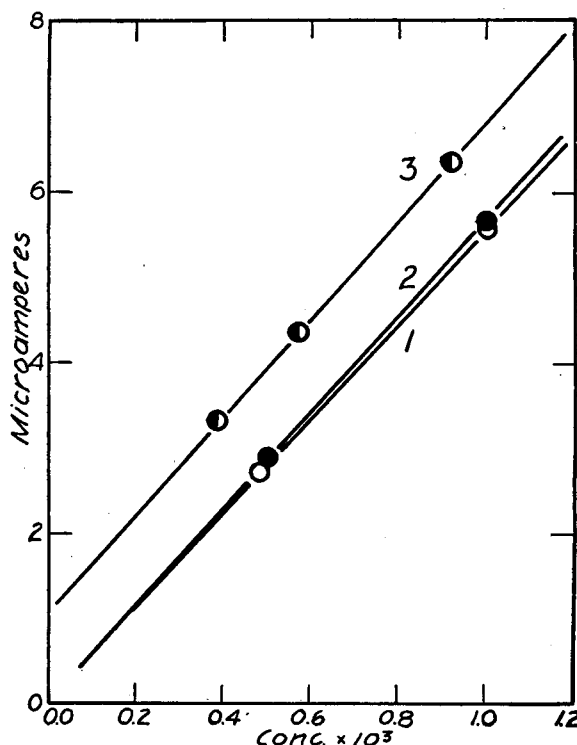
Figure 6. Diffusion Current Constants for Barium

In calcium chloride (1), lithium chloride (2), and magnesium chloride (3), measured at −2.05 volts

Figure 5. Comparison of Barium Waves in Calcium Chloride and Magnesium Chloride as Supporting Electrolytes

1. Residual current in 0.05 M CaCl$_2$
2. Residual current in 0.05 M MgCl$_2$
3. 1.00×10^{-3} M barium in 0.05 M CaCl$_2$ corrected for residual current
4. 0.91×10^{-3} M barium in 0.05 M MgCl$_2$ corrected for residual current
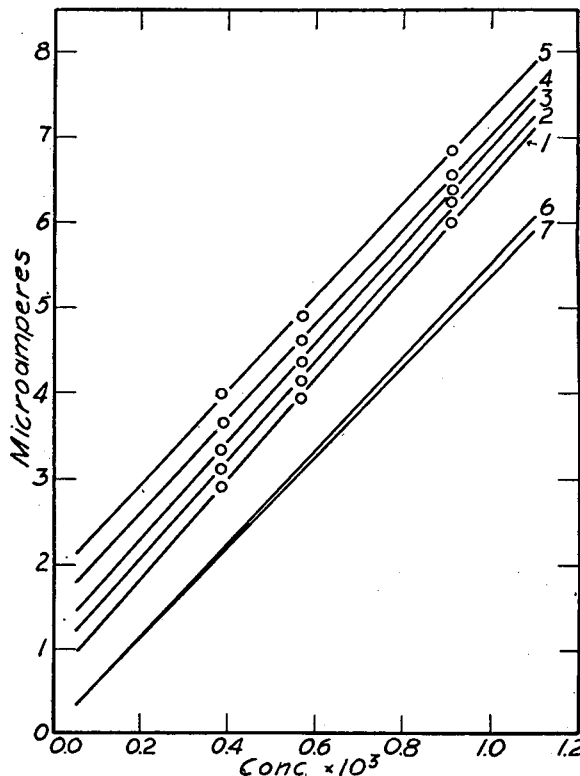
Figure 7. Diffusion Current Constants for Barium in Magnesium Chloride and Calcium Chloride Measured at Different Potentials

In 0.05 M MgCl$_2$, measured at −2.000 volts (1), −2.025 volts (2), −2.050 volts (3), −2.075 volts (4), and 2.100 volts (5)
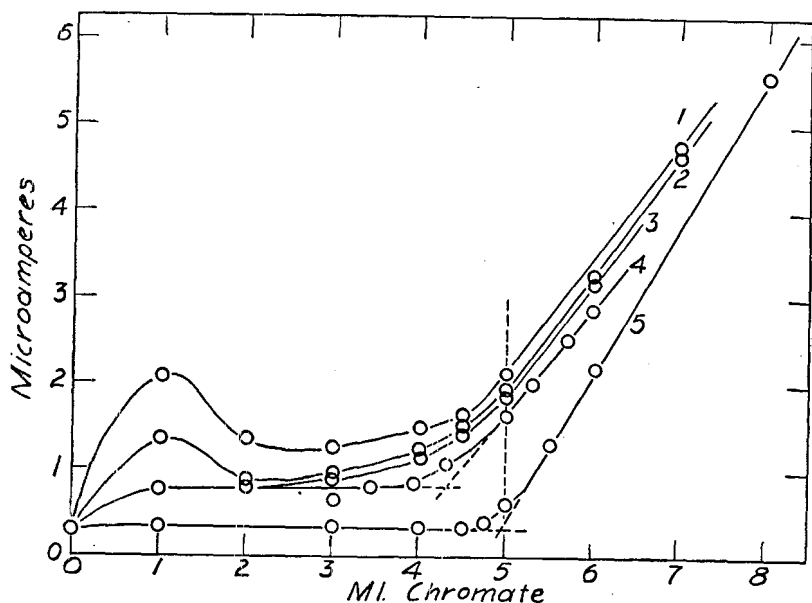In 0.05 M CaCl$_2$, measured at −2.000 volts (6), and −2.100 volts (7)

Figure 8. Titration of 50 Ml. of 0.001 M Barium Solution in 0.1 M Lithium Chloride with 0.01 M Chromate

1. Titration performed with 2-minute interval after addition of chromate
2. 4 min.
3. 6 min.
4. 30 min.
5. 27 hours

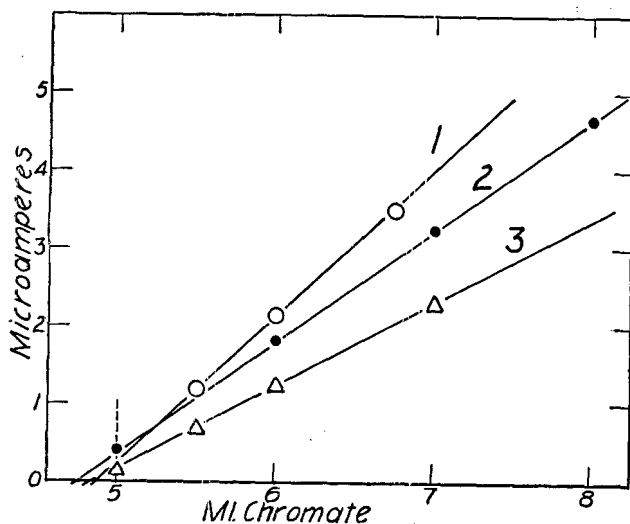Corrected for dilution but not for residual current. Applied potential −1.4 volts

Figure 9. Titration of 50 Ml. of 0.001 M Barium Solution

In 0.1 M lithium chloride and 20% (1), 30% (2), and 50% (3), ethanol with 0.01 M chromate. Corrected for residual current and dilution. Applied potential −1.4 volts

current line has an ascending slope. On the other hand, in calcium chloride as supporting electrolyte the diffusion current line, after correction for the residual current, has a descending slope which is normal at these high negative potentials. This is demonstrated in Figure 5.

The relation between i_d and C for the barium current in 0.05 M magnesium chloride at −2.05 volts is given in Table I. It is seen that as the barium concentration increases the value of i_d/C decreases. The diffusion current constant in magnesium chloride is greater than in calcium or lithium chloride. A further correction can, however, be applied. In Figures 6 values of i_d are plotted against C at −2.05 volts. Here it is seen that the slope of all three curves is substantially the same. Therefore if one assumes that the diffusion coefficient of barium is the same

in magnesium chloride as in calcium chloride, and that the constant difference between the two can be applied as a correction, then i_d becomes proportional to C (Table II). This general type of correction can be applied at any point in the "apparent diffusion current region" of the barium wave in magnesium chloride, as shown in Figure 7.

Calcium chloride is the best supporting electrolyte for the measurement of the diffusion current of the barium ion in aqueous medium.

AMPEROMETRIC TITRATION OF BARIUM WITH CHROMATE

The amperometric titration of barium with chromate was first carried out by Kolthoff and Pan (2, 3, 5). Chromate was found (4) to give four reduction waves in 0.1 M potassium chloride with the half-wave potentials of −0.3, −1.0, −1.5, and −1.7 vs. saturated calomel electrode. The first wave at −0.3 volt increased its relative height with decreasing concentration, but the wave at −1.0 volt gave values of i_d proportional to C. Kolthoff and Pan were able to titrate 0.01 M barium with chromate successfully in aqueous media, but at greater dilutions encountered poor accuracy.

The amperometric titration of of 0.001 M barium with 0.01 M potassium chromate in 0.1 M lithium chloride was carried out at −1.4 volts. In aqueous media a supersaturated solution of barium chromate was formed and several hours were required to obtain equilibrium values. In Figure 8 are plotted the results in a series of titrations which were carried out with 2-, 4-, 6-, and 30-minute intervals between the addition of chromate and the current reading. One titration was carried out by adding various amounts of chromate to barium solution and shaking for 27 hours before making a reading. It is seen that an accurate determination can be accomplished only by the latter impractical procedure.

In order to lower the solubility of barium chromate and to increase its rate of precipitation, titrations with chromate were carried out in 20, 30, and 50% ethanol. Current readings were taken immediately after addition of reagent and mixing in the cell (Figure 9). The titration in 20% ethanol is 2.4% low, in 30% it is 5.0% low, and in 50% it is 3.4% low. This deviation probably is due to coprecipitation of barium with the barium chromate or formation of basic barium chromate. The titration in 20% ethanol in the presence of a buffer with a pH of the order of 5 to 6 deserves further study.

Titrations of 0.0001 M barium with chromate in ethanol-water mixtures were not successful, the end point occurring 10% before the theoretical end point.

Table II. Correction for Anomalous Diffusion Current of Barium in 0.05 M Magnesium Chloride at π = −2.05 Volts

Barium Concn. M	i_d in MgCl₂ $\mu a.$	$\dfrac{i_d}{\text{in CaCl}_2}$ (Calcd.) $\mu a.$	$i_d(\text{MgCl}_2) - i_d(\text{CaCl}_2)$ $\mu a.$	$i_d(\text{Corr.})/C$ $\mu a./M \times 10^1$
3.85×10^{-4}	3.33	2.20	1.13	5.72
5.68×10^{-4}	4.38	3.24	1.14	5.70
9.10×10^{-4}	6.38	5.22	1.16	5.74

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Preparation of Dried Latex Films

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A method is described for the preparation of compounded and uncompounded rubber films from latex by casting. With alkaline latexes the method involves the use of a carbon dioxide–water vapor atmosphere in the initial stages of the surface skin formation to render it porous and permeable to water evaporation. As a result of this permeability the films obtained are smooth, and free of the cracks, ridges, and bubbles encountered with the usual means of film casting. Because of absence of imperfections, films prepared by this technique show appreciably higher tensiles than those prepared as controls without the carbon dioxide–moisture treatment. The method described has been applied successfully to the casting of rubber films from GR-S, Hycar, neoprene, and natural latexes. Excellent films as large as 32 × 14 inches, and up to 0.05 inch thick, have been cast without difficulty.

VARIOUS technical applications of latex call for the formation of a latex film and its drying by evaporation of the water in which the rubber is dispersed. The same problem is encountered also in the preparation of dried latex films, both uncompounded and compounded, for film testing for tensile, elongation, and other properties. Very frequently the preparation of such films is complicated by the development of surface cracks and ridges in the drying films (1–6) which mar the appearance of the films, detract from their strength, and make testing difficult and uncertain. These imperfections in the films generally arise from the formation of impervious surface skins on the drying latex. Such impervious skins lead to shrinkage and subsequent cracking of the films on the one hand, and to bubble formation on the other. The result is that the preparation of dried latex films by this method becomes a very slow process, which yields as a rule films of inferior appearance and quality.

It was found in this laboratory that many of the difficulties encountered in the preparation of latex films by evaporation can be overcome by appropriate control of humidity in the initial drying stages, and the use of an agent which prevents formation of the impervious surface skins on the drying latex. The agent found to be most suitable with alkaline latexes for the latter purpose is carbon dioxide gas. By utilizing moisture and carbon dioxide in a definite technique, films can be prepared from various latexes which are smooth and uniform in thickness and possess improved appearance and properties.

The purpose of this paper is to describe the technique developed for preparation of dried latex films by casting, and to give some results for tensile and elongation obtained on GR-S, Hycar, neoprene, and natural latexes.

EQUIPMENT FOR FILM PREPARATION

Molds. Most of the latex films prepared in this laboratory are cast in glass molds 30 cm. (10 inches) wide by 37.5 cm. (15 inches) long. The molds are made of double-strength window glass as a base, to which are cemented 1-inch strips of single-strength window glass to form a cavity 8 inches wide, 13 inches long, and 0.085 to 0.095 inch deep. Sodium silicate is used as a cement to seal the border strips to the base. Any excess silicate adhering to the glass is removed to leave a clean surface for the latex film.

For some work a larger mold is used, prepared in the same manner, but having a cavity 32 × 14 × 0.09 inches. This mold was made originally to find out whether a film of this size can be cast successfully, and to obtain a larger number of test strips from a single film. It was found that films of this large size can be prepared just as satisfactorily as smaller films. However, large glass molds are generally difficult to handle and level in a drying oven and they tend to warp with time. To obviate the last difficulty a metal mold was also tried. It proved satisfactory in remaining true in shape and in accelerating film drying by better transfer of heat, but it was too heavy to handle conveniently, and gave some trouble in transmitting surface imperfections in the metal surface to the cast rubber film surfaces.

Drying Ovens. The oven employed for the setting of the latex films is a Thelco incubating oven made by the Precision Scientific

Company. This oven is equipped with double doors, the inner ones of glass through which the film can be observed, and is large enough to accommodate the 32 × 14 inch mold. It is a gravity convection type oven fitted with top and bottom vents, and is equipped with automatic temperature control.

The final drying or curing of the films was originally conducted in ordinary laboratory ovens of the gravity convection type. At present these operations are conducted in forced draft circulation ovens. The latter types of oven give a more uniform distribution of heat and better temperature control than the ordinary ovens, and hence more rapid and uniform drying or curing of films is possible in them.

Carbon Dioxide Supply. The carbon dioxide gas used for conditioning the latex surface is ordinary cylinder gas. It is fed to the setting oven by means of rubber tubing entering the oven through one of the top circulation vents.

Exhaust Pump. To expedite water removal in the latter stages of the film setting, a small exhaust pump is attached to the top of the oven. By means of this pump the air circulation of the oven can be increased sufficiently to reduce the time of the film setting to about one half to one third of the time normally required without good air circulation.

STEPS IN FILM PREPARATION

The film casting and setting are carried out in the incubating oven kept at 50° C. Before the latex is poured into the mold several preliminary operations must be carried out. The first involves placing the mold, thoroughly cleaned and dried, in the oven and leveling it on the oven shelf. It is imperative for good results that the mold be level; otherwise the drying is not uniform and the thickness of the film is variable. Any open space on the oven shelf around the molds should further be covered with glass or metal plates, so that the flow of heat is directed through the mold, and convection of gases around the mold is prevented. Failure to observe this precaution results frequently in considerable crazing of the film in the initial drying stages.

The next step is to saturate the oven with water vapor to prevent rapid drying of the latex during the initial setting period. Such rapid evaporation promotes too rapid a skinning over of the latex, and leads to cracking and ridge formation. The moisture saturation of the oven is accomplished simply by placing a pan of warm water on the bottom shelf of the oven below the mold.

When the oven is suitably saturated with moisture, and the mold is at oven temperature, the latex is poured into the mold. The latex introduced may be straight latex without any additions, or latex that has been compounded. Care should be exercised in pouring the latex, so as to avoid introduction of bubbles. The amount introduced depends upon the thickness of film desired, and can be estimated by trial. In any case, the volume poured into the mold must be sufficient to cover the entire bottom of the mold to a depth sufficient to give the requisite thickness of dry film. It will depend upon the size of the mold used and the solids content of the latex.

Immediately after the introduction of the latex the oven is closed, the bottom vents are plugged, and carbon dioxide admis-

sion is started through the top vent. To prevent the carbon dioxide stream from hitting and disturbing the latex surface, it is best to place a glass baffle plate between the carbon dioxide entrance and the latex mold. By this means the gas is dispersed throughout the oven without impinging directly on the latex. Unless this precaution is observed the latex surface is disturbed, and the resulting film develops a rippled appearance.

The initial rate of carbon dioxide entrance must be sufficient to ensure rapid saturation of the oven chamber with this gas, so that formation of the impervious film surface, which is detrimental to good film formation, can be prevented. Within a short time of the carbon dioxide entrance the latex surface acquires a lighter hue, and the rate of carbon dioxide flow can then be diminished. Under the further action of the carbon dioxide, and in the presence of the water vapor, the surface gradually assumes a dull cast which is indicative of the formation of the desired type of surface skin. Completion of this phase in the skin formation is evidenced by a uniform spread of this dull cast over the entire latex surface. At this stage the carbon dioxide addition is stopped, the pan of water is removed from the oven, the bottom vents are opened, and the film is left undisturbed for an hour or more before the drying rate is accelerated by initiating gentle air circulation through the oven by means of the suction pump. At the end of some time the rate of air circulation can be increased substantially, and continued until the film is set. "Setting" is said to be completed when the film of rubber is sufficiently rigid to be removed from the mold and handled for final drying.

As an uncompounded latex film dries in setting, it undergoes a regular series of transformations. First it loses its opalescence and takes on a dull appearance. After a while the film starts to develop a transparency analogous to viscous gel. Finally, as evaporation proceeds and the film begins to set, the transparency disappears slowly, and the film starts to become opaque. Setting is complete when the opacity permeates the entire film. The film is ready then to be removed from the mold. With compounded latexes these changes are more difficult to observe because they are masked by the opacity of the compounding ingredients.

Experience has shown that it is best to remove the films from the molds right after setting rather than to let them dry completely in the molds. When left in the molds until dry the films tend to develop strains, and show a tendency to stick tenaciously to the glass surface. Strongly adhering films can be loosened by introducing a little water under the film edge, but then the films have to be redried, and the strain damage is done. It is best, therefore, to complete the final drying of uncompounded films, or drying and curing of compounded films, in a separate oven, preferably one with forced draft circulation. On final drying the uncompounded rubber films become transparent, whereas the compounded films are opaque. Uncompounded films are dried at 100° C., whereas compounded films are dried and cured at whatever temperature is necessary.

The above technique of film preparation has been applied successfully to GR-S, Hycar, neoprene, and natural latexes. Apparently the size of the film is no limitation, for small as well as large films of excellent quality have been prepared. Although in all cases the general procedure followed was as described above, the actual periods of time to which films of different latexes were subjected to various phases of the process varied. Table I summarizes the conditions found to be optimum for preparation of uncompounded latex films. Generally 1 to 1.5 hours of carbon dioxide treatment are required for all latexes tried except Neoprene 571 and natural latexes. Neoprene 571 coagulates completely when subjected to carbon dioxide for 1 minute, and hence only about a 30-second flash admission of the gas can be used. However, even this short exposure to the gas is sufficient to yield an improved film of neoprene. With natural latexes the approximately 1-hour exposure to carbon dioxide has been found necessary when the ammonia content of the latexes was low. On the other hand, when the ammonia content was appreciable satisfactory skinning over conditions could be obtained in as short an exposure to carbon dioxide as 5 minutes. Excessive carbon dioxide treatment in the latter instances resulted in the formation of a coagulated gel which resembled very closely the type of gel obtained on treatment of such latexes with appreciable quantities of ammonium salts.

The optimum time of moisture treatment was found to range from 0.5 to 1.5 hours, depending on the latex. In turn, the drying time of about 1 hour without air circulation has been found necessary because in its early stages the surface film is too weak to withstand rapid evaporation. Once this surface film toughens somewhat, the rate of water removal can be accelerated.

In all cases except natural latex approximately 12 to 14 hours are required to set a film. With natural latex the setting time is very rapid, and at the end of about 4 hours the latex film is not only set but dry as well. Generally films once set are dried at 100° C. for about 24 hours. The maximum tensiles are usually observed at the end of this drying period in all cases except natural latex, which showed better tensiles at the end of the 4-hour setting time than on subsequent drying.

With compounded films the carbon dioxide–moisture treatment periods are essentially the same as those given in Table I for uncompounded films, but the setting times are longer, usually about 24 hours for Type III latex. Furthermore, compounded films do not seem to require subsequent drying in addition to the heating required to obtain optimum cure—i.e., generally about 1 to 1.5 hours at 100° C.

Table I. Details of Film Preparation Procedure for Uncompounded Latexes

Latex	Type III	Hycar OR-30	Hycar OR-40	Neoprene 571	Natural Latex
Solids, %	36–40	30	40	50	60
Time of CO_2 treatment, hours	ca. 1	1–1.5	1–1.5	30 sec.	5 min. to ca. 1 hour
Time of moisture treatment, hours	ca. 1	1–1.5	1–1.5	ca. 0.5	ca. 1
Time of drying without circulation, hour	ca. 1	ca. 1	ca. 1	ca. 1	ca. 1
Time of drying with circulation, hours	10–12	10–12	10–12	10–12	ca. 2
Total setting time, hours	12–14	12–14	12–14	10–12	ca. 4
Final drying time at 100° C., hours	ca. 24	ca. 24	ca. 24	ca. 24	Generally none
Total time for film prepn., hours	ca. 36	ca. 36	ca. 36	ca. 36	ca. 4

RESULTS AND DISCUSSION

The use of carbon dioxide and moisture regulation in film preparation was found in every case to yield films superior to those prepared by other techniques. Controls run on the various latexes under conditions which were similar, but without carbon dioxide and moisture present, yielded in general films of poor appearance and with surface cracks. On the other hand, the films prepared as described were smooth and without the imperfections ordinarily observed and showed in every case higher tensile strengths than the corresponding controls. Table II shows data on uncompounded films to substantiate this statement. It is evident that the carbon dioxide–moisture treatment leads to a film not only improved in appearance but also of better physical characteristics. The two factors may well be connected, for a film without strains, cracks, ridges, or bubbles should be able to resist tension better than one with flaws.

The action of carbon dioxide in yielding satisfactory skin formation on latex film surfaces suggests that other acidic gases as well may be suitable for this purpose. This is actually the case. Hydrogen chloride gas was found to work well on Type II latex. However, from a corrosion standpoint carbon dioxide is to be preferred to other acidic gases. Alkaline gases should also be applicable to acidic latexes prepared with cationic emulsifiers.

Table II. Tensile Data on Uncompounded Films

| | New Method | | Control | |
| Latex | Tensile | Elongation | Tensile | Elongation |
	Lb./sq. inch	%	Lb./sq. inch	%
Type III	800-1200	1400-1700	700	1600+
Hycar OR-40	760	2000+	390	2000+
Neoprene 571	2800	1200	1520	1000
Natural	1800	1200	1500	1200

Preparation of rubber films from latex by the method described here generally does not require any preliminary treatment of the latex, such as thickening. However, indications are that the latex must be sufficiently alkaline to absorb some carbon dioxide for satisfactory surface skin formation. When the alkalinity is too low good film formation is difficult. This is exemplified by attempts to produce films from Type II latexes. Such latexes have as a rule relatively low pH's and their tendency to good skin formation in presence of carbon dioxide is poor. When, however, the pH is raised to about 10.5 by addition of sodium hydroxide the formation of satisfactory films in presence of carbon dioxide is considerably improved.

Many compounded latex films have also been prepared by the carbon dioxide–moisture technique. Their behavior was found to be essentially similar to that of the uncompounded films. As an example may be cited the preparation of a rubber film from Type III latex compounded with Vanderbilt Dispersion C-199. This compounded latex skinned over in 1 hour in presence of carbon dioxide and water vapor, and set and dried in 24 hours. On curing at 100° C. for 1.5 hours the film gave a tensile of 2200 pounds per square inch and an elongation of 800%.

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Laboratory Evaluation of Oil Deterioration

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Detailed consideration is given to the physicochemical variables involved in the deterioration of engine, turbine, and transformer oils and those factors which are significant in service. It is possible therefrom to establish the conditions most suitable for laboratory tests. Behavior of engine lubricants in the ring-belt area cannot be studied in tests designed for measuring crankcase-oil stability but the investigation requires specially adapted high-temperature experiments. Limitations are discussed as well as difficulties in correlating test results with field data. It is concluded that the laboratory methods should be employed not so much to predict the useful life of an oil as to provide a relative rating and information as to the fundamental chemical nature of a series of oils.

DETERIORATION of oils in service may have serious consequences in a number of ways. Rarely, however, can it be said that such effects arise from loss of the oil involved; thus, in used oil from normal engine service perhaps 97% of the oil molecules remain unaltered, but the other 3% exert so profound an effect that complete oil change is advisable.

In general, deterioration of oils is associated with oxidation, although cracking and volatilization should not be ignored. Three principal types of oxidation products are recognized: sludge, acids, and saponifiable substances that may interfere with proper functioning of mechanical parts or of the oil itself. Filter-screen clogging, oil-passage plugging, ring sticking, and lacquer deposition are all familiar problems in engine operation which result from sludge or high-molecular-weight oil and fuel oxidation products. Acids are objectionable in engines if corrodible bearing metals are present; in turbine oils they may lead to emulsion formation; in transformer oils, to impairment of insulation. Saponifiable materials include a large variety of organic substances such as esters, lactones, anhydrides, peroxides, and metal soaps. Some of these substances are fairly innocuous, but most of them will lead to a viscosity increase of the oil, thereby altering its behavior as a lubricant, while some, such as peroxides and metal soaps, may act as catalysts for further oxidation or bearing corrosion. It is impractical in laboratory apparatus to simulate all the service factors that lead to these various secondary effects of oil deterioration. It is more logical to study the primary process with the expectation that, if certain oxidation products are present, they may under some service conditions be involved in one or more of the secondary phenomena.

GENERAL REQUIREMENTS OF LABORATORY TESTS

Oil can be oxidized very simply by placing it in an open beaker on a hot plate. This very simplicity is misleading, however, as many factors affect both the magnitude and direction of the changes which occur. Rate of chemical reaction is determined by concentration of reactants, temperature, and catalysis. A laboratory test should have these three variables adjusted to agree with those of service if the results are to be strictly comparable. Unfortunately, exact correspondence is seldom attained and a compromise is made, most frequently to reduce the duration of the test. Often, too, the important variables that apply to service are not properly defined. For example, it is still impossible to specify precisely the local temperatures encountered by an oil in an engine.

Temperature. In adopting laboratory test conditions, choice of the means of acceleration should receive very careful attention. In general, test temperatures should not be raised more than is necessary; to do so may affect the nature (as well as the rate) of the reactions. Furthermore, the effect of water upon deterioration of turbine oils is not evaluated if temperatures are so high that it cannot be present in significant amounts. The type of deposits formed on engine bearings depends upon temperature; thus, laboratory corrosion tests at high temperature may fail to indicate oil performance in an engine operating at much lower temperatures.

Catalysts. Catalysts alter the mechanism of chemical reactions by breaking down a process of high activation energy into steps requiring less energy which, of course, proceed more

rapidly. Hence, misleading results may be obtained unless proper choice of catalysts is made. The degree of acceleration should not be too severe and, if possible, the catalyst should match or resemble materials actually present in service. Mineral oils possess a certain amount of natural anticatalytic activity or catalytic tolerance which is, however, exceeded if very much catalyst is present, and the oil then appears to be unstable. Furthermore, use of large amounts of a particular catalyst encourages the addition of artificial anticatalysts to the oil, which may be specific for this particular catalyst but of little value in service where catalytic conditions are more varied.
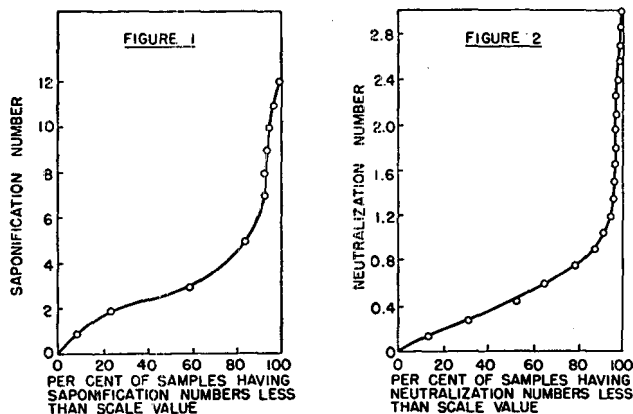
Aside from materials added to the oil, catalysts and inhibitors are formed spontaneously by the oxidation process itself as exemplified by the autocatalytic and autoretardant reactions obtained with various oils (43). The volatile acidic oxidation products are active pro-oxidants especially when metals are present, and may be termed "catalyst promoters." Efforts should therefore be made to retain volatiles during a test to some degree.

Concentration. After temperature and catalytic acceleration, the only rate-increasing factor is concentration of the reactants. Obviously, the nature of the oil at the start of the test is fixed, so that only the oxygen concentration can be raised. The latter at first seems unobjectionable, and generally is accomplished by the substitution of pure oxygen for air. However, if the oxygen pressure is increased above atmospheric, bomb-type tests are required which incur mechanical difficulties, particularly in keeping the oil saturated with oxygen. Furthermore, extreme compression may fundamentally change the reaction mechanism; thus, to avoid explosions, which would obviously occur by a different mechanism than the slow oxidation, common safety regulations require that no oil be employed to lubricate fittings on oxygen cylinders. Conditions in bomb tests do not remain constant, inasmuch as the oxygen pressure decreases as reaction proceeds and other gases— viz., carbon dioxide—accumulate. If the acceleration attained by using oxygen at atmospheric pressure is not sufficiently great, it would therefore be preferable to attain the desired rate by a moderate increase in temperature rather than by further increase in pressure.

In order to measure the intrinsic stability of the oil it is imperative that the liquid be kept saturated with oxygen; minor variations in gas supply will then not be a rate-determining factor. Diffusion is a slow process, but moderate bubbling or stirring will maintain an adequate oxygen concentration, as the absolute consumption of oxygen is not high unless the test is greatly accelerated. However, contrary views have been expressed in the literature (24, 25), the contention being that extreme agitation is required but in a manner that does not cause excessive loss of volatile oxidation products.

Severity of Tests. In laboratory testing the degree of deterioration to be achieved should be carefully considered and, in

general, agreement with service should be established. Wilson and Kemmerer (47) analyzed approximately one hundred "complaint" samples of used engine oils which undoubtedly represent more than average severity of oil deterioration. The cumulative relative frequency distribution curves for a number of used oil properties (Figures 1 to 4) show that only 10% of the samples had a saponification number above 6 and an acid neutralization number above 1.0, whereas the extreme high values were 12 and 3.0, respectively; analogous values for naphtha-insolubles were 1.4 and about 3.4%. The tendency of the used oils to decrease in viscosity (due to dilution) was greater than the tendency to increase in viscosity by oxidation. There is thus doubt as to the importance sometimes attached to viscosity increase in laboratory tests.

The above data indicate the severity encountered in normal automotive engine service. Certain laboratory engines are much more severe (saponification numbers for the 36-hour Chevrolet test on undoped oils reach values as high as 40 to 50, neutralization numbers about 10), but these, too, are testing devices and correspondence with actual service must be established. However, as they are coming to be accepted as specification tests for lubricating oils, it may in some cases be well to make chemical laboratory tests equally severe.
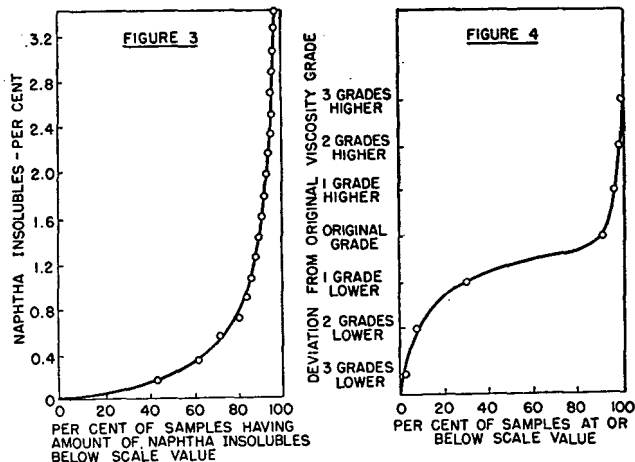
The available information on severity of service for turbine and transformer oils does not permit a statistical analysis but merely indicates the range to be expected. In Figure 5 are given the data of Petersen (33) which show the increase in neutralization number with years of service for an uninhibited turbine oil. In practice the oil is usually changed when a neutralization number of about 1 is reached. The data for transformer oils in Figure 6 are less precise but indicate an acidity of about 4 as the maximum encountered in very long service periods. Many operators of
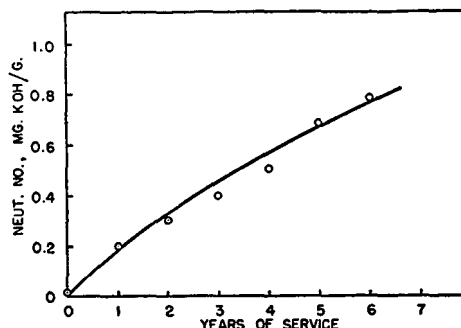

Figure 5. Deterioration of Turbine Oils in Service

Table I. Distribution of Oxygen Absorbed by Three Base Stocks Derived from Different Crudes

(Reaction temp., 150° C. Final degree of oxidation, approx. 28 ml. oxygen per gram of oil. All oils SAE 40 grade)

Fraction of Absorbed Oxygen Recovered as	Naphthenic Crude	Mixed-Base Crude	Paraffinic Crude
Water, %	65.7	65.8	64.7
Carbon dioxide, %	13.6	12.9	10.9
Volatile acids, %	1.4	1.0	3.1
Free acids			
Oil-soluble, %	4.6	9.0	8.0
Oil-insoluble, %	2.3	0.4	0.9
Total, %	6.9	9.4	8.9
Combined acids			
Oil-soluble, %	14.7	18.7	19.6
Oil-insoluble, %	6.8	1.1	2.5
Total, %	21.5	19.8	22.1
Alcohol, %	2.5	2.1	2.7
Carbonyl, %	1.4	4.9	2.6

Table II. Degree of Oxidation of Oil-Insoluble Oxidation Products

Oil	% Carbon	% Hydrogen	% Sulfur	% Nitrogen	% Oxygen (by Diff.)	Neutralization No.	Saponification No.
30 V.I. naphthenic	74.62	7.81	2.80	0.61	14.16	80	351
45 V.I. naphthenic	74.18	7.56	2.42	0.50	15.34	80	362
70 V.I. naphthenic	74.05	7.66	1.69	0.29	16.31	93	410
95 V.I. mixed base	75.3	7.7	0.6	0.45	15.95	..	..
100 V.I. paraffinic	76.8	7.3	0.61	0.22	15.07	..	373
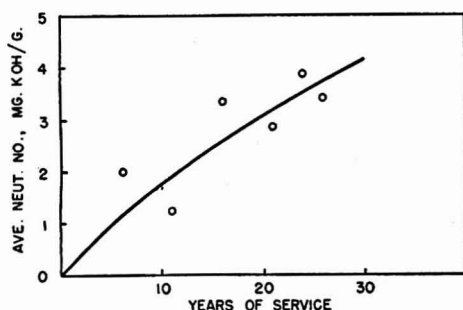
Figure 6. Deterioration of Transformer Oils in Service

electrical equipment change the oil when a neutralization number of 1 is reached.

From the degree of oxidation encountered in service, it would seem possible adequately to fix the duration or severity of laboratory tests. However, this is possible only when the variables of temperature, catalysis, and concentration are correctly chosen. Furthermore, complications are introduced by the fact that rate of oxidation is not always constant with time but may be either of the autocatalytic or retardant type. Thus, the rate curves for two oils A and B may be concave upward and downward, respectively, crossing some time after the start of the test; if evaluated at some standard time which happens to be before the intersection point, A would be regarded as superior to B; after this point the relative ratings would be reversed.

LABORATORY TESTS FOR EVALUATING ENGINE OILS

Oxygen-Absorption Method. Once a satisfactory apparatus has been developed, conditions can be varied in many ways which will, in turn, largely determine the results obtained. It is not difficult to choose an apparatus for studying the primary oxidation process, for this is most convincingly done by measuring the rate of oxidation. If, however, the results of oxidation are to be studied, the problem becomes more complicated. Thus, in the case of a study of bearing corrosion, it is necessary not only to control the variables affecting oxidation, but to simulate the engine conditions prevailing at the bearing surface which lead to

shear in the oil layer and deposition or removal of protective coatings.

Of the many advantages in studying the primary oxidation process by the oxygen-absorption method, the chief one is that an unambiguous measure of net oxidation is obtained. Furthermore, the data afford a complete and continuous record of the behavior of the oil from the beginning of the test. From the shape of the rate curve, it is possible to judge the type of oil or of antioxidant present and to evaluate the effect of a catalyst or anticatalyst more precisely than by following the change in oil properties. Of course, effect of oxidation on the oil itself is more directly involved in determining performance characteristics but, as indicated below, correlation of used-oil properties with oxygen-absorption data has already been established.

Many types of oxygen-absorption apparatus have been described by Dornte (14), Fenske (17), Larsen (28), and Von Fuchs and Diamond (43). It has often been argued that the requisite equipment is too complicated and occupies too much space to be useful for routine work. However, current views are changing. The photograph in Figure 7 shows an eight-unit automatic machine which occupies a small space (3 × 2 feet of floor space) and is not difficult to operate. The initial cost is moderate; maintenance may be a problem unless a skilled instrument man is available for occasional repairs or adjustments, but this is not a serious obstacle to most modern petroleum laboratories.

Oxygen Balance. Oxygen-absorption measurements make it possible to establish an "oxygen balance" between the amount of oxygen consumed and that appearing in various oxidation products; this affords considerable information on the type as well as the absolute rate of oxidation. Such an investigation has been
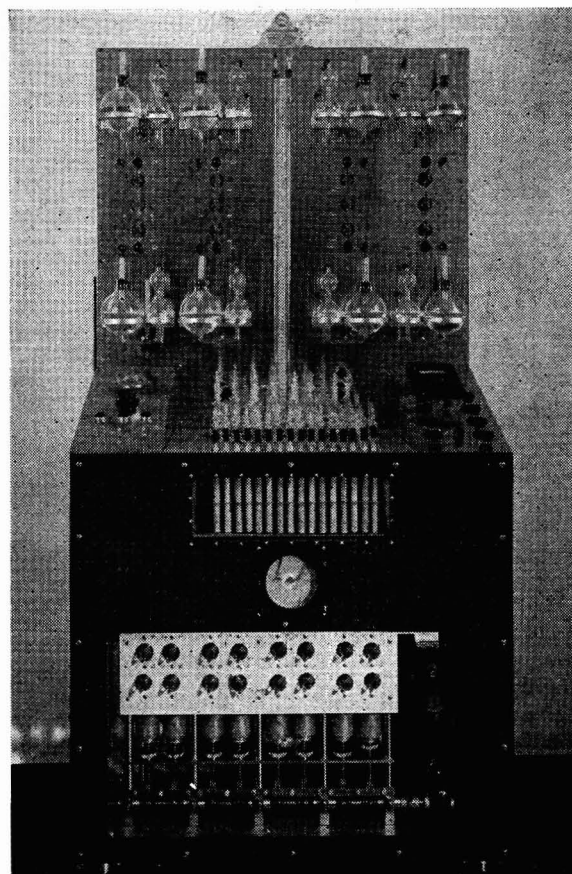

Figure 7. Eight-Unit Automatic Oxygen Absorption Apparatus

Table III. Engine and Turbine Oil Tests

Test	Ref. No.	Stability or Corrosion	Method of Contacting	Air or oxygen	Rate of circulation or stirring	Oil temp., °C.	Test duration, hours	Sample size	Catalysts	Stability[b] Measured by:	Special Features and Comments
Engine oil tests											
Sligh	(36)	S	Diffusion	Oxygen	...	200	2.5	10 g.	None	Naphtha-insol.	Limited oxygen supply
Davis	(13)	S		Oxygen	...	175	c	10 g.	Metal naphthenates	Induction period	Uses modified Sligh flask
Bridgeman	(8)	S		Air		175	24	160 g.	None	Used-oil analyses	Lack of positive aeration
Caterpillar	(46)	C		Air	60 r.p.m.[d]	132	c	400 ml.	Cd-Ag bearing segment	......	Bearing sample rotated
British Air Ministry	(18)	S	Air or oxygen bubbled through the oil	Air	15 liter/hour	200	Two 6-hour periods	40 ml.	None	Viscosity increase and carbon residue	Cooling cycle between two oxidation cycles
Indiana	(35)	SS		Air	10 liter/hour	171.7	c	300 ml.	9 ft. of 18-gage iron wire	Time to form 10 and 100 mg.[e] naphtha-insol./10 g. oil	......
Continental	(46)	S		Air	10 liter/hour	171.7	48c or 72	160 ml.	300 sq. cm. steel, 20 sq. cm. Cu	Naphtha-insol., viscosity, carbon residue	Uses Indiana test equipment but adds catalyst
Sohio	(10)	S, (C)		Air	30 liter/hour	154.4	20, 65	160 ml.		Used-oil analyses, lacquer deposition on steel tube	Catalyst based on area of metal exposed in engine
Penn State	(21)	S, (C)		Air	10 liter/hour	175	20, 50, 80	100 ml.	8.25 sq.in. iron, 15.75 in. No. 40 Cu wire	Used-oil properties and lacquer deposition on glass plate	Similar to Sohio test
Asphaltization	(16)	S		Air	10 liter/hour	171.7	c	400 ml.	Cd-Ag bearing segment	Time until oil will no longer flow at 80° F.[f]	Uses Indiana test equipment, very severe
Underwood	(32)	S, C	Oil sprayed through air	Air	...	162.8	5, 10, 15c	1500 ml.	Copper, bearing segments, and soluble catalysts[g]	Used-oil analyses	Oil sprayed through air
Stirring Indiana	(25)	S, (C)	Air or oxygen beaten into oil	Air	1300 r.p.m.	165.6	72	250 ml.	5 sq. cm. Cu	Neut. No. and naphtha-insoluble value	Air beaten into oil
MacCoull	(29)	S, C		Air	3000 r.p.m.	176.7	10h	125 ml.	10 sq. cm. Fe / Copper and bearing[g]	Used-oil analyses	Oil forced between bearing surfaces
Corrosion and stability	(45)	S, C		Air	600 cc./min. 1310 r.p.m.[d]	184	3, 5	225 g.	Bearing segment	Used-oil analyses	Bearing wiped by felt
Sunbury	(42)	(S), C		Air	680 cc./min. 680 r.p.m.[d]	160	20c or moreh	400 ml.	3 × 1¼ × 1/32 inch Cu and bearing segments[g]	Used-oil analyses	Bearing sample rotated
Thrust bearing corrosion	(40)	C		Air	50 cc./min. 2400 r.p.m.	Various	20	35 ml.	Bearing segments[g]		Positive washing of bearing surface by oil shear
Turbine oil tests											
Turbine oil stability test	(44)	S	Bubbled	Oxygen	3 liter/hour	95	c	300 ml.	0.5 sq. cm. Fe/g.	Interfacial tension and neut. No.	Volatile products retained. Contains water
Pope and Hall	(33)	S, C	Stirred	Moist oxygen	850 r.p.m.	100	c	250 ml.	0.5 sq. cm. Cu/g. / Steel and Cu	Interfacial tension and neut. No.	Volatile products retained. Measures stability and rusting

a Most tests allow for use under other conditions if desired.
b In tests measuring corrosion, degree of corrosion is determined by weight loss.
c Length of test depends upon stability of oil sample under test.
d Corrosion specimen used as stirrer.
e For oils having 10-mg. times over 100 hours viscosity increase is also measured.
f If at 400 hours oil is still fluid, test is terminated and viscosity and naphtha-insoluble content measured.
g Iron used in constructing apparatus also acts as catalyst.
h Bearing removed, cleaned, and weighed at intervals during test.
i Corrosiveness of an oil is measured by temperature at which appreciable corrosion first occurs.

carried out both on pure hydrocarbons (28) and on oils (17), but additional study has led to the conclusion that this approach is not worth while on a routine basis. Thus, oils vary surprisingly little in the direction in which oxidation proceeds, with the exception of the solubility of the oxidation products. For example, the three base stocks derived from the crudes listed in Table I produce almost identical quantities of the various deterioration products. Although the total fixed and combined acids (saponifiable substances) are about the same for each of the oils, the portion soluble in the oil varies. Because the oil-insoluble products are highly oxidized, as indicated by the oxygen contents shown in Table II, the quantity of oxidized substances remaining in the oil is markedly reduced by their removal.

From the quantity of oxygen absorbed it is generally possible to calculate the saponification and neutralization numbers, amount of water and carbon dioxide found, etc., as accurately as they can be determined analytically. Thus, once the rate curve is established, it is only necessary to determine the sludge value to obtain complete information on the oxidation of the oil, and a great deal of time can be saved.

Apparatus for Determining Effects of Oxidation. Most of the recent tests have been devised primarily to measure the results of oxidation, particularly bearing corrosion, which has been a serious problem in operation of heavy-duty engines. The salient features of many of the tests are summarized in Table III. An evaluation of each is impractical, because data are not available for a complete comparison, but a few general comments may be made. First, the usual oil analyses—e.g., neutralization number—do not accurately measure corrosivity. Furthermore, polarization at the metal surface plays an important role in determining the extent of chemical attack, and consequently shear in the oil adjacent to the bearing should be comparable to that occurring in the engine. This is accomplished in the thrust bearing corrosion machine by employing a Kingsbury-type bearing operating under load (40); in the corrosion and stability apparatus (45) intimate contact and removal of passivating layers are achieved by a felt pad wiping the surface. In other machines, such as the MacCoull (29), the oil is forced between closely fitted bearing surfaces; in the Underwood (32) a jet of oil impinges on the bearing.

All the corrosion-type tests described have the limitation that deterioration is judged by the results, such as weight loss of a bearing, and not by the primary oxidation process. They should therefore be considered in this light. The present trend is also to evaluate stability during the corrosion test by the increase in neutralization number, sludge content, etc., which, though of immediate concern, are still definitely less satisfactory experimental criteria than the amount of oxygen consumed. It would seem
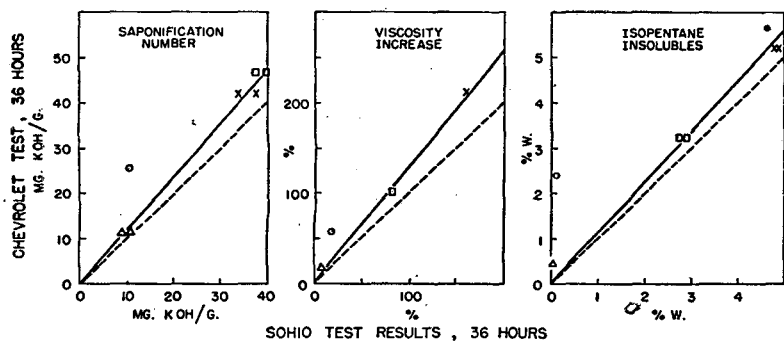
Figure 8. Comparison of Sohio and Chevrolet Results

Table IV. Corrosion as a Function of Temperature in the Thrust Bearing Corrosion Machine

(Fixed conditions: Cu-Pb bearings, 125 lb./sq. inch thrust, 2400 r.p.m.)

Oil	Loss in Mg. Per Sq. Cm. at:						
	110° C.	120° C.	130° C.	140° C.	150° C.	160° C.	170° C.
Detergent oil C	0.1	24.3	28.1	76.9	74.5	a	..
Oil C + inhibitor I	..	..	..	22.3	3.6	1.0	0.8
Oil C + inhibitor II	0.0	0.1	0.2	0.4	0.4	0.5	0.4

a Runs failed owing to excessive corrosion and overheating.

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logical to determine oxygen absorption and bearing weight loss in a single test, so as to provide simultaneously a complete measure of stability and the effect of oxidation on bearing corrosion and sludge formation.

Temperature of Tests for Engine Oils. Although crankcase-oil temperatures generally fall in the range of 75° to 140° C., it is seen (Table III) that most laboratory tests are conducted at 170° C. or higher, chiefly to reduce the time required for testing. It is also argued that, because a small part of the oil is in the much hotter region of the ring-belt area, test temperatures should be chosen as a mean of the temperatures in an engine. For example, the Sohio method (10), employing a test temperature of 154.4° C. and iron and copper catalysts, gives good correspondence with the Chevrolet engine operating at a crankcase-oil temperature of 138° C. (cf. Figure 8). However, the Chevrolet test itself represents a high degree of acceleration and further increase in severity of conditions—e.g., to temperatures above 170° C.—may not be justified.

The dependence of reaction rate on temperatures is not linear but a very steep exponential function, and precise extrapolation over a wide temperature range is uncertain. Furthermore, deterioration of oils is not a simple elementary process but a complex sequence of many consecutive and concurrent reactions which are accelerated to different degrees by a marked rise in temperature. Unless this is avoided, the over-all course of oxidation, cracking, polymerization, dehydration processes, etc., may be drastically altered, and hence the lowest temperature giving results in a reasonable time is preferred; 150° C. appears suitable, as it affords a catalyzed reaction time of about 40 hours for a stable oil. As discussed below, it is believed that high-temperature deterioration cannot be adequately evaluated in tests designed primarily to measure stability in the crankcase and should be studied by methods specifically designed for the purpose.

The use of excessively high test temperatures is considered even more objectionable for the corrosion-type tests than for the oxygen-absorption type, because formation of surface films is often involved in protecting the bearings. In Table IV data recorded for an inhibited detergent oil show that the bearing weight loss is higher at a lower temperature, probably because the inhibitor does not become active until the higher temperature is reached.

A counterpart is seen in engines, for oils have been examined that pass certain high-temperature tests but fail at lower temperatures. Other factors may be involved, but the results illustrate the need for careful attention to temperature. A single test at an arbitrarily chosen high temperature may be misleading and study at several temperatures may be required.

Catalysis in Tests for Engine Oils. Catalysis is perhaps the most important and the least understood of the factors determining the applicability of laboratory tests. Its importance is recognized by the fact that almost without exception all recent tests employ catalysts that vary from oil-soluble metallic soaps to free metals in powder, wire, or sheet form. In a recent article (26) it was shown that all possible relative ratings can be obtained for three different oils merely by varying the concentration of a single catalyst. The caution which must be used in adopting hard and fast standard conditions is therefore obvious.

A priori, it would seem preferable to add accelerators in the form of elementary metal rather than as soaps, inasmuch as the oil would then have a chance to form catalytically active soluble components in the same manner as in an engine (unless catalysis is purely heterogeneous, in which case solid metal is certainly required). Furthermore, "passivators" that may be present in the oil would be able to function by forming protective films as in an engine, no matter what the mechanism of catalysis. Choice of catalyst is a controversial matter, as some investigators have obtained considerable success using soaps. In one sense the reacting system is thus oversimplified, with the metal-oil interface eliminated, and the effect of passivators cannot therefore be shown. Nevertheless, the action of "deactivators" which precipitate or form complexes with metal ions may still be made evident, whether soaps are added initially or formed during an experiment.

An important type of accelerator is "crankcase catalyst," the oil-insoluble ash-containing solids that accumulate in engine oils during use. Although large quantities of this material can be obtained by centrifuging used oils, it would be unsuited as a standard because of variation from batch to batch. Efforts have therefore been made to prepare a "synthetic crankcase catalyst" by mixing various pure substances. In Table V, crankcase

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Table V. Development of Synthetic Crankcase Catalyst

(Oxidation temperature, 150° C.)

Catalyst	Time to Absorb 1800 Ml. of O₂ per 100 Grams of Oil, Hours		Ratio B/A
	Oil A	Oil B	
0.5%w crankcase catalyst (California)	2.10, 2.22	23.4	10.9
0.5%w crankcase catalyst (Illinois)	2.15	20.9	9.7
0.1%w (FeCl₃ + solids from oxidized oil)	2.37	27.5	11.6
0.005% FeCl₃ (anhydrous)	3.26	28.9	8.9
0.1% FeBr₃ (anhydrous)	2.10, 2.15	23.7	11.1
0.003% FeCl₃ (dissolved in isopropyl alcohol)	2.34	24.7	10.6
Iron naphthenate (30 p.p.m.)	3.5	11.0	3.1

Table VI. Comparison of Ferric Chloride with Crankcase Catalyst

Catalyst	Time to Absorb 1800 Ml. of O₂ per 100 Grams of Oil at 150° C., Hours					
	Oil A	Oil B	Oil B-1	Oil B-2	Oil B-3	Oil B-4
0.5%w crankcase catalyst	2.10, 2.22	23.4	17.9	4.2	30.6, 31.8	5.3
0.003%w ferric chloride a	2.34	24.7	106	4.0	>100	19

Oils B-1 and B-3 contain additives; all others are undoped.

a Added dissolved in isopropyl alcohol.

Table VII. Transformer Oil Tests

Test	Ref. No.	Method of Contacting	Air or oxygen	Rate of circulation	Oil temp., °C	Catalyst	Amount of Sample	Time, hours	Tests on Oxidized Oil	Special Features and Comments
A.S.T.M. sludge test, method A	(1)	Diffusion-oxidizing atmosphere over sample	Air	0.5 liter/hour	120	Copper	25 ml.	72, 168, 336	% sludge at end of three test periods	Tentative method
A.S.T.M. sludge test, method B			Oxygen	Diffusion, pressure vessel	140	None	50 ml.	24	% sludge	Oxygen under 250 lb./sq. inch pressure, tentative method
Snyder life test	(2)		Air	1 cu. ft./hour	120	None	500 ml.	Variable	Visible sludge in oil	Modifications being considered (see Clark-Snyder test)
Clark-Snyder sludge test	(37) (12)		Air	1.5–2 cu. ft./hour	120	With or without Cu	25 ml.	Variable	% sludge at several periods	Plot rate of sludge formation
Baader test	(5)		Air	Open container	95	Copper	...	48	Saponification value	Very mild for good oil
Moloney test	a		Air	Open test tube	150	With and without Cu	...	8	No sludge permitted. Color change	Evaluation by color change
Matthis test	(31)		Air	Open container	Variable—e.g., 170, 200	None	40 ml.	Variable—e.g., 5, 10	Time and temp. when sludge appears	Used many years in France
Official Swedish test	(39)		Oxygen	Open container in oven	120	None	...	70	Kissling tar value	
Brown-Boveri test (Swiss)	(39)		Air	Open container	112	Copper (cotton thread)	...	168	Sludge, acid value	Also measure decrease in tensile strength of cotton
Stäger test	(38)		Air	Open container	112	None	1200 ml.	100, 200, 300, 500, 1000	Sludge	
Gemant test / Evers and Schmidt test	(19) (16)		Air / Oxygen	Closed vessel / Closed vessel	145–155 / 120 or 150	None / Vanadium and ferric oxides	130 ml. / ...	Variable 2 hours or more / 45	Oxygen consumption / Oxygen consumption	Adds air to maintain constant pressure / Used by Siemens Co. (Germany)
B.S.I. test Brit. Stand. Spec.	(9)	Oxygen or air through the oil	Air	2 liters/hour	150	Copper	100 g.	45	Sludge	Use water-cooled condenser to retain volatile products
Anderson-Asea test / International Electrotechnical Com. test	(3) (3)		Oxygen / Oxygen	Closed system / Closed circulating system	110 / 100	Copper-iron / Copper-iron	...	50 / 50, 75, 100	% sludge, % acids / Oxygen consumed, sludge, acids	Widely used Swedish test / Also includes effect of electric field
Michie test	(3)		Oxygen	Closed circulating system	150	Copper	...	45	Sludge, acids	
Revised Butkov test	(11)		Oxygen	4–5 liters/hour	150	Copper	...	Variable	Sludge, acids, saponifiable	Russian test

a Moloney Electric Co., St. Louis, Mo.

catalysts separated from engine drainings obtained in two different geographical areas are compared with several synthetic mixtures containing iron halides, as these compounds were found to be the most active components of the oil-insolubles (27). Several synthetic combinations give good agreement with the engine catalyst on undoped oils, but in Table VI it is seen that a representative one fails rather badly on the two doped oils B-1 and B-3 (of the SAE Chevrolet test program). A synthetic crankcase catalyst has not yet been found which rates doped oils in the same order as does the natural catalyst. The insolubles derived from the engine may act as a catalyst reservoir, slowly feeding active material into the oil in a way difficult to reproduce with synthetic mixtures.

If elementary metals are to be used as catalysts, iron would first seem the most logical choice. However, it is actually a poor one, for it has been found impossible to obtain sheets or wire of reproducible activity; reduced iron powder is more uniform but has unique properties of its own and presents difficulties in obtaining intimate contact with the oil. Copper, being reproducible and active, is used very extensively as a catalyst and often seems to give results comparable to engine ratings when moderate amounts are taken. In Figure 9 curves show the catalytic effect of various amounts of copper and iron. Obviously, employment of an amount of copper corresponding to the steep part of the curve would lead to irreproducibility; a minimum of 1 sq. cm. per gram of oil is most logical. In view of the practical difficulties in using other types of catalysts, this would seem to provide the best catalytic conditions for testing engine oils. However, a single catalyst of this type may be counteracted by a specific anticatalyst which occasionally will be found without beneficial effect in actual operation. Experiments with single metals are valuable in fundamental studies on the nature of special oils, but are perhaps not so well adapted as is a complex catalyst for predicting their relative ratings in service.

HIGH-TEMPERATURE OXIDATION

The work of many investigators discussed above has been directed at the deterioration of oils under conditions prevailing in the crankcase of an engine, and the information now available is of great value in alleviating difficulties arising from this source—e.g., sludging and bearing corrosion. However, the behavior of the small amount of lubricant that is present at any time in the upper cylinder is important here with reference to the urgent problems of ring sticking and lacquering, and, indeed, most of the deterioration may occur in this region (especially in dry-sump, air-cooled aircraft engines). Conditions here are so different, particularly with respect to temperature (265° C. being typical), that supplementary experiments are clearly warranted.

The change in mechanism of oxidation with large increase in temperature and the difficulty of precise extrapolation have been mentioned; moreover, simple cracking and volatilization become significant factors. If reaction rate were doubled for every 10° C. rise in temperature according to the usual rule, an oil which oxidizes severely in 40 hours at 150° C. would oxidize to the same degree in about 2 minutes at 250° C. As most engines operate at crankcase temperatures below 150° C., the contrast between deterioration in the crankcase and on the piston is even more striking. Deposits removed from ring grooves, piston skirts, etc., invariably show a high oxygen content, indicating that severe oxidation has occurred.
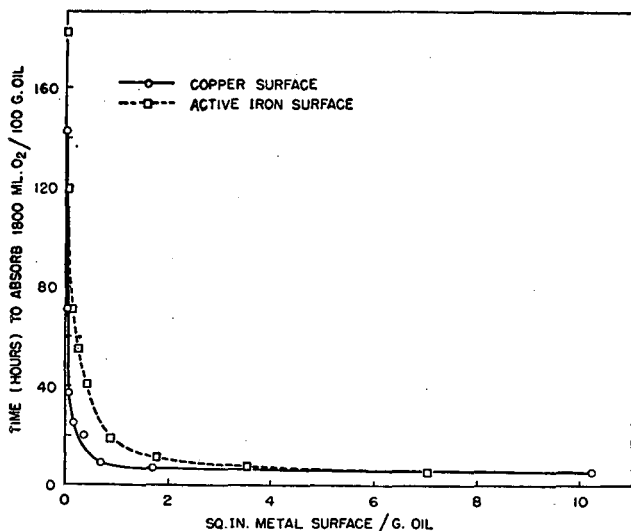
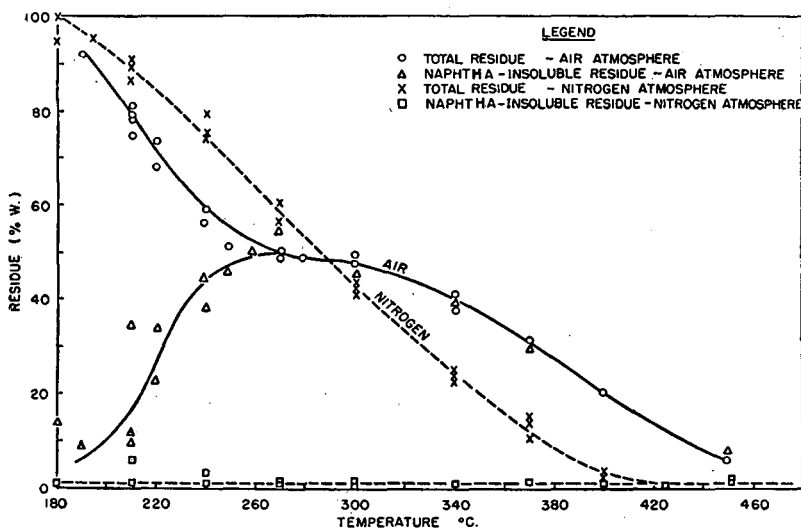Figure 9. Oil Stability *vs.* Catalyst Surface Exposed

Figure 10. G.M.C. Lacquer Plate Test

Residue *vs.* temperature, S.A.E. 60 grade extracted oil

because of the difficulty in controlling the flow of oil over the heated surface. A modification which consisted of a slowly rotating bar and a glass-cloth spreader was still unsatisfactory.

Finally, it was found that a modification of a lacquer-plate test originally developed by General Motors could be used to give quantitative data.

A short cylinder is welded into the circular depression of the original lacquer plate, which effectively prevents the oil from creeping off. The plate is accommodated in a small gas-tight cell constructed of iron pipe and fittings. Any specified atmosphere may be maintained in the cell by passing compressed gas through the apparatus. Heat is supplied by electric windings and a preheating coil in the gas inlet, making it possible to conduct experiments at temperatures up to 450° C. Readings of temperature are taken on a thermocouple mounted just below the plate.

A 0.2-gram drop of oil is placed on the lacquer plate, which is then heated for 1 hour at the designated temperature. After heating, the amount of residue is determined as well as its solubility in boiling naphtha. The insoluble residue is an extensively oxidized hard lacquer similar to that found on pistons, while the soluble residue is still an oily liquid. The data of Figure 10 show that, in an air atmosphere, a typical oil is covered to a completely insoluble lacquer at 270° C.

As shown by the dotted line (Figure 10), when this oil is heated in an inert atmosphere, it gradually distills away until, at a temperature of 400° C., none remains. At any lower temperature the residue is still an oil, as indicated by complete solubility in naphtha. On the other hand, two changes occur when oxygen is present: the total amount of residue is different; and, more important, the residue becomes insoluble at a relatively low temperature. In the low-temperature range, oxidative cracking takes place when oxygen is present and less total residue is formed. At higher temperatures, however, the oxidation products polymerize to high-molecular-weight lacquers which volatilize less readily than does the unoxidized oil.

At very high temperatures oil and oil oxidation products volatilize with almost equal ease, the most deleterious effect of oxygen being that the residue is converted to a solid instead of remaining as a liquid. When the temperature is sufficiently high, all the deposit is burned off. It therefore follows that there is an optimum temperature for the formation of piston deposits. Gruse and Livingstone (*20*) as well as Rosen (*22*) report that the location of piston deposits depends considerably on the temperature, a gradient, of course, existing from top to bottom of the piston.

An undesirable feature of the lacquer-plate tests is that they are static, and therefore the ability of an oil to wash deposits away is not measured. Thus, no improvement is observed when a detergent is added to the oil. Furthermore, conventional oxidation inhibitors have little effect in these tests and volatility has a rather pronounced effect on the magnitude of the changes observed. Nevertheless, some information on the fundamental nature of deposit formation is obtained and the potential capacity of base oils to produce lacquerlike material is indicated.

LABORATORY TESTS FOR DETERIORATION OF STEAM TURBINE OILS

Unlike engine oils, turbine lubricants are subjected to long periods of continuous operation at moderate temperatures, and it should therefore be easier to duplicate their deterioration in the laboratory. It is necessary, however, to accelerate the laboratory test, because turbine oils are expected to remain in service for thousands of hours without appreciable change.

Relatively little has been written on the evaluation of oils under high-temperature conditions. Rosen (*23*) describes a hotbar test wherein oil is dropped onto the hot end (343° C.) of an inclined bar and permitted to flow down toward the cooler portion. It is demonstrated that intermediate conditions give maximum deposition of deterioration products. Thwaites (*41*) describes a somewhat similar apparatus consisting essentially of a metal funnel with a groove on its inner surface down which the oil under test is allowed to flow. Good correlation is claimed between a C.F.R. engine demerit rating and the weight of deposits formed from a given amount of oil flowing down the cone when heated to 250° C. A unique high-temperature test apparatus described by Matthijsen (*30*) consists of a circular saw rotating at 2800 r.p.m. which is immersed in oil heated to a temperature of 230° C. and flings it in fine drops against the heated sides of the oil container. High-temperature baking tests are described by Beall (*7*) and van Hinte (*22*), wherein oil is heated in aluminum cups to 270° to 290° C. for 30 minutes or more, after which evaporation losses and the usual sludge, acid values, etc., are determined.

The Rosen aluminum bar was studied but little success was achieved in obtaining reproducible quantitative data, primarily

Because turbine lubricating systems often contain water as a contaminant, provision should be made to maintain the oil in a wet condition during the test; in particular, the temperature should not be too high to permit the presence of water. Rusting of iron surfaces will then occur which will, in turn, affect the catalytic activity of the metal. Volatile oxidation products, which affect the reaction, must also be retained to some extent.

With turbine oils even mild oxidation is undesirable, and a test that indicates incipient oxidation is required. Interfacial tension between oil and water responds to very small amounts of polar oxidation products and changes appreciably even during the induction period of inhibited oils. Neutralization number serves to indicate more extensive oxidation and is taken as a criterion of the total useful life of the oil. Sludge would also be important, but fortunately is not formed to a significant extent in well-refined turbine oils before the neutralization number has reached an appreciable value. Two tests recently described by Von Fuchs, Wilson, and Edlund (44) and by Pope and Hall (34) appear to give adequate consideration to such factors as temperature, agitation, presence of moisture, metals, etc. (cf. Table III). In both tests the beneficial effect of inhibitors and the rust protection afforded by modern turbine oils are clearly shown. It is noteworthy that volatile oxidation products accelerate oxidation considerably, further demonstrating the need for avoiding excessively high temperatures.

It is difficult to correlate the new tests for stability of turbine oils with service, because several years may elapse before oxidation begins. Because of the wide variation in operating conditions, an exact ratio of life in a given turbine to life in any test cannot be established. Laboratory results are sensitive to variations in technique, type of glass, position of catalyst coils, etc., which have no counterpart in service operation. These considerations do not, however, detract from the significance of the relative ratings of oils, but rather emphasize the scrupulous care that must be taken in devising laboratory methods.

LABORATORY TESTS FOR DETERIORATION OF TRANSFORMER OILS

In addition to the effect of temperature, catalysis, and oxygen concentration, the possibility that the electrical field also affects deterioration of oils in transformers must be considered. The literature on this subject is contradictory but, a priori, little effect of the field on chemical kinetics would be expected. Chemical reactions may be accelerated by electron bombardment, but these occur only at discharge voltages which are not attained in a well operating transformer. Current alone also seems to be without effect, as oil undergoes little change over a period of several years in transformers where air is completely or partially excluded by means of inert gas blankets or "conservator" tanks. It is, of course, possible that, although the electrical field will not accelerate oxidation, it may have an influence on the products of oxidation. Anderson (3) reporting on the very excellent work at the Asea Materials Laboratory (Sweden) concludes that the electrical field (10,000 volts, 60 cycles) affects both the amount and solubility of the sludge as well as the acid values of the soluble and insoluble components. The electric field had no effect on the rate at which the oil absorbed oxygen. On checking the experimental data, the magnitude of the effects ascribed to the electric field is found to be relatively small and it is concluded that no serious error would be introduced by its omission in a laboratory test.

Sludge is the most troublesome of all the deterioration products of transformer oil because it interferes with oil flow and cooling (the chief function of the oil). It is seen from Table VI that with very few exceptions determination of the amount of sludge formed in a given time is the principal object of the tests. The acid value of an oil in service is often taken as a criterion for changing oil, not because of the intrinsic properties of the acids, but because they indicate that oxidation has occurred and sludge may

be formed. Acids may attack the insulation or, in extreme cases, corrode copper cooling coils, but on the whole they are not considered to be very serious contaminants. Water, particularly in the presence of sludge, is a serious problem. Most frequently, moisture results from atmospheric condensation or leaks in cooling coils or transformer cases and is not a factor that can be controlled by oil quality.

Inasmuch as with transformer oils, as with other oils, the main object is to prevent over-all oxidation regardless of the nature of the secondary products, the oxygen-absorption type of apparatus is believed to be the most useful. Tests of this type were described by Anderson (3) and more recently by Balsbaugh and co-workers (4, 6). Not only inherent stabilities but also changes in chemical and electrical properties—e.g., conductance—were determined. Differences are thus revealed which depend upon many factors and are not apparent in simple tests. The type of oxygen-absorption apparatus is not critical, although the mercury valves used by the Swedish investigators have been found to influence the reaction; glass valves are suitable and can be easily constructed.

Test Temperature for Transformer Oils. According to the American Standards Association, the hottest spot in a continuously operating transformer never rises above 95° C., and the average copper temperature to 85° C. The maximum allowable oil temperature varies from 70° C. for continuous operation to 85° C. for recurrent short-time overloads. However, a test temperature of 70° C. would be too low for practical purposes even with catalyst and pure oxygen. Balsbaugh (6) determined the time required for a well-refined oil to absorb 2000 cc. of oxygen per kg. of oil in the presence of copper catalyst at various temperatures to be as follows:

Temperature, ° C.	75	85	95	105	115
Time, hours	950	660	220	60	25

A temperature of about 100° C. would, therefore, seem to be the minimum for a test of practical duration. Anderson concludes that 100° C. is undoubtedly the highest permissible test temperature for a transformer oil on the basis of laboratory studies of oils of known service record; Balsbaugh shares this conclusion.

Catalysis in Laboratory Tests for Transformer Oils. Transformer oils in service are in contact with iron (silicon steel), copper, varnish (which may contain soaps as driers), cotton, wood, cardboard, silk, nylon, and glass. Of these copper undoubtedly has the greatest catalytic activity and most tests employ this metal. As in the case of engine oils, for adequate reproducibility the amount of copper used must be sufficient to fall on the flat part of the curve (Figure 9). Iron may also be included but, unless used in very large quantities, it will have less effect than does the copper. The ratio of copper to iron in a transformer also favors the omission of iron as a catalyst (Anderson gives a surface ratio of 4 to 1 for warm iron to copper in one particular design, which is not enough to compensate for the difference in activities). Variations in the type of varnish, insulation, etc., render an evaluation of these factors uncertain, and it is unwise to include such materials in standard tests.

Severity of Tests for Transformer Oils. The data of Figure 6 indicate that a neutralization number of 2 to 4 would be representative of maximum deterioration in service, which would require between 1000 and 2000 ml. of oxygen per 100 grams of oil. Comparable data on sludge values are not available but, in one large installation where the oil appeared to be badly deteriorated, a sludge content of 0.2% was found.

It is questionable whether electrical properties of the oxidized oil other than dielectric strength—e.g., conductance or power factor—should be measured, as they do not critically affect the performance of oils in transformers.

CONCLUDING REMARKS

Factors that determine the choice of conditions used in the laboratory evaluation of engine, turbine, and transformer oils

have been discussed without reference to actual data correlating the laboratory tests with performance of the oils in the field. Although correlation would be desirable, service conditions are so varied that unequivocal conclusions cannot be drawn. The various test conditions suggested are based on an analysis of the fundamental aspects of the problem and are directed toward providing reproducibility. Although the significance of the absolute values obtained in laboratory tests may thus be questioned, they probably give a reliable relative rating of oils and an analysis of the variables that affect deterioration in practice. If it is desired merely to know how well an oil behaves in an engine, probably the simplest thing to do is to run it in the engine.

The way in which test results are interpreted is highly important. Wide experience which one laboratory may have accumulated on a particular test often accounts for the success obtained there, whereas other investigators may find the same procedure inadequate.

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Frequency Errors in Timing with Electric Clocks

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ELECTRICALLY driven stop clocks are commonly used in the laboratory for measuring time intervals. Obviously, the precision with which time intervals are measured can be no better than the control of the frequency of the alternating current used to drive the clocks (2). When the commercial power line is used as a source of current, as is usually done, errors may result from the deviation of frequency from its nominal value of 60 cycles per second. Over periods of several hours or more, errors in timing, expressed on a percentage basis, usually become small, because the generators at the power house are subject to adjustments which maintain the average frequency over a long period of time very close to 60 cycles per second. Larger errors are to be expected if the time interval is of the order of a few minutes or less.

For several years clocks operating from the power line have been used in connection with calorimetric studies at the University of Pittsburgh. To evaluate the errors in timing resulting from this practice, the authors have performed the experiments described in this paper.

EVALUATION OF FREQUENCY ERROR

Magnetically driven precision tuning forks of 60-cycle frequency are commercially available. The signal generated by the fork may be fed into a simple power amplifier, the output from which may be used to drive one or more clocks (1). By suitable comparison of two clocks, one driven by current from a tuning fork and the other from the power line, one can evaluate the errors involved in using the latter.

The measurement of time intervals using electrically driven stop clocks is subject to uncertainty if the frequency of the current supply deviates from 60 cycles per second. To evaluate the frequency error in using the commercial power available in Pittsburgh, the authors have compared two clocks, one driven by the power line, and the other by a magnetically driven precision tuning fork. The maximum deviations noted for various time intervals are less than 0.2%. Probable errors are about 0.05%.

A Type 815 60-cycle fork, obtained from the General Radio Company, was used in this study. The average frequency of the fork was determined by comparing a clock driven by the fork with the time signal broadcast from the National Bureau of Standards. The time of observation varied from 1 to 1.5 hours. The frequency of the fork was determined to be 59.9860 ± 0.0005 cycles per second at 25° C. (This value differed insignificantly from the frequency given by the manufacturer.)

The temperature coefficient of frequency of the fork was given by the manufacturer as approximately 0.0005% per Centigrade degree. Tests confirmed the fact that the influence of temperature is extremely small. The fork was mounted in a wooden box equipped with a thermometer. At all times the temperature was within a few degrees (5° at most) of 25° C., so that no correction for the temperature dependence of frequency seemed necessary.

The clocks used in the comparisons had second hands that completed one revolution in 10 seconds. The two clocks, one driven by the power line and the other by the fork, were placed side by side and photographed at 50-second intervals for a period of an hour or more. By using a photographic method any errors resulting from starting or stopping the clocks were eliminated. The exposure time was always 0.01 second. The photographs were sharp and the reading of the clocks could be estimated to 0.01 second. The experiments were carried out at various times of the day and over a period of several months.
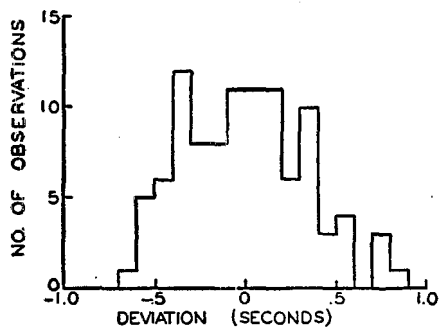
Figure 1. Frequency Distribution Curve for Deviations Observed in 100 Independent (Not Overlapping) Time Intervals, Each of 10-Minute Duration

The differences between the times indicated by the two clocks, as read from the film, were plotted as a function of time, and the resulting graphs used to provide the data from which Figures 1, 2, and 3 were constructed. The deviations occurring in 100 independent 10-minute intervals were found, and the number of periods having deviations within consecutive 0.1-second intervals were plotted against the deviations to give the frequency distribution curve shown in Figure 1. Figures 2 and 3 were constructed in a similar manner from 201 periods of 5 minutes and 219 periods of 1 minute. The least counts in these cases were 0.05 and 0.01 second, respectively. The probable errors of single measurements computed (3) from the tabulated deviations are shown in Table I.

Table I. Probable Errors of Single Measurements

Interval	No. of Observations	Probable Error	
Min.		Sec.	%
10	100	0.23	0.038
5	201	0.12	0.040
1	219	0.025	0.042
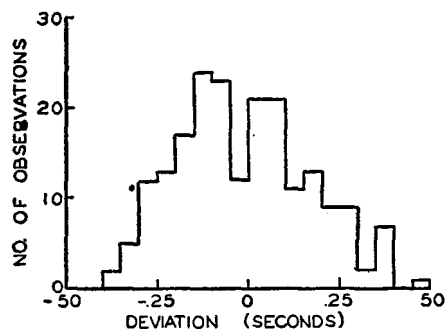
Figure 2. Frequency Distribution Curve for Deviations Observed in 201 Independent (Not Overlapping) Time Intervals, Each of 5-Minute Duration

Supplementing the information contained in Table I, the authors have noted that the maximum deviations observed in this study are 0.14, 0.16, and 0.17% for the 10-, 5-, and 1-minute intervals, respectively. Furthermore, although the data have not been quantitatively analyzed for time intervals smaller than 1 minute or larger than 10 minutes, some qualitative conclusions may be drawn. On a percentage basis frequency errors will be about the same for time intervals of a few seconds as for time intervals of 1 to 10 minutes' duration. (For these cases the error in starting and stopping the clock would undoubtedly be the principal one.) For time intervals of approximately 2 hours or longer the percentage errors would be smaller than those listed in Table I, inasmuch as data clearly show that the periodic adjustment of the generators to produce an average frequency of 60 cycles per second is accomplished in less than an hour.

The data shown in the frequency distribution curve have been examined with the idea of determining how often frequency deviations lead to errors in timing equal to or greater than 0.1%. For the number of observations indicated, 10% of the readings were in error by 0.1% or more for 10-minute intervals, 8.5% for 5-minute intervals, and 13% for 1-minute intervals.

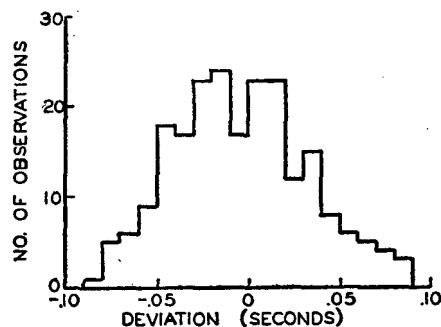It is believed that the data presented, while by no means ex-

Figure 3. Frequency Distribution Curve for Deviations Observed in 219 Independent (Not Overlapping) Time Intervals, Each of 1-Minute Duration

haustive, will give some idea of the magnitude of frequency errors expected in clocks operated from the commercial power line. It appears that for most experiments requiring reasonably precise time measurements, the clocks operated from the power line are adequate.

While, strictly speaking, the results of this study are applicable only in the Pittsburgh area, the conclusions may be of interest to others with similar problems, working under more or less comparable conditions. There is no reason for believing the control of frequency of the Pittsburgh power supply to be unique and, accordingly, the frequency errors revealed in this study are probably representative of those to be expected in using the line

current available in any large American city. The procedure employed can, of course, be immediately used in other areas to ascertain the reliability of the local power source for operating electric clocks.

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Spectrochemical Determination of Copper

In Copper-Zinc and in Copper-Nickel Alloys

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Procedures are described for the determination of copper, as the major constituent, from the ratio of the intensities of a pair of its lines. The method is suitable for the determination of copper in the range 70 to 97% in copper-zinc alloys and 90 to 99% in copper-nickel alloys. The importance of excitation conditions and of size and shape of electrodes is shown. A possible cause of the effect is suggested.

HASLER and Kemp (5) have reported that copper in aluminum bronze can be determined in the range 75 to 90% from the ratio of the intensities of two copper lines. This method of analysis has also been used by Calker (1) for the determination of bismuth and magnesium as minor constituents in various matrixes. Calker found that the same line pair can be used with different matrixes, although the working curves change as the matrix element is changed.

In order to determine whether this rule also applies to major constituents, in cases other than aluminum bronze, a study was made of copper in copper-zinc and copper-nickel alloys. These systems were chosen because only solid solutions are involved and thus possible difficulties due to segregation are avoided.

EQUIPMENT

The laboratory equipment included the grating spectrograph (6), Multisource unit (4, 5), and comparator-densitometer (3) supplied by the Applied Research Laboratories.

The conditions under which the spectra were obtained are shown in Table I.

PHOTOMETRIC PROCEDURE

The Eastman spectrum analysis No. 1 film was processed in the ARL-Dietert film developing machine (7) which is equipped with a thermostat to hold the developing trays at 70° F. The films were developed, with mechanical agitation, for 3 minutes in Eastman D-19 developer, immersed in a 3% acetic acid solution short-stop for 10 seconds, and fixed in Eastman x-ray fixing bath for 30 seconds.

The film was calibrated by use of a two-step filter (2) using an iron arc. A gamma of 2.1 was obtained for the range 2850 to 2950 Å. No background correction was necessary.

EXPERIMENTAL PROCEDURE

The experiments of Hasler and Kemp (5) on aluminum bronze were repeated on a series of copper-zinc alloys, whose composition is shown in Table II.

These samples were in the form of strips about 3 inches long, 1 inch wide, and 0.06 inch thick. These were used as upper elec-

trodes on a Petrey stand, with a lower electrode of the National Carbon Co. specially purified graphite. Hasler and Kemp, using Multisource settings of $C = 5\mu f.$, $L = 100\mu h.$, and $R = 10r.$, which give a critically damped discharge, found that the intensity ratio of the 2882.9 Å Cu I line to the 2441.6 Å. Cu I line varied with percentage copper. Using these conditions, this variation was not found with the copper-zinc alloys. This indicates that the other elements present have a profound effect on the concentrational sensitivity of the lines of the major constituent. This study could not be extended to the copper-nickel alloys, because a nickel line at 2441.7 Å. interferes.

A study of the spectra of these samples produced by the oscillating discharge obtained with the Multisource settings listed in Table I showed that the spark line 2884.383 Å. varies in intensity relative to the arc line 2882.934 Å., as the percentage of copper varies. Using the ratio of the intensities of these lines, a satisfactory working curve for the determination of copper in brass in the range 70 to 97% was obtained (curve A, Figure 1).

Table I. Conditions for Obtaining Spectra

Multisource settings	Spectrograph settings
Capacitance, 2 microfarads	Spark gap, 3 mm.
Inductance, 50 microhenries	Slit width, 60 microns
Resistance, 0.4 ohm	Upper electrode, alloy
Output voltage, 940 volts	This was the positive electrode
Initiator at, continuous	Lower electrode, 0.25-inch graphite
Prespark, 10 seconds	rod tapered to hemispherical tip
Exposure, 10 to 15 seconds	

Table II. Composition of Copper-Zinc Alloys

Sample, No.	Copper, %	Zinc, %	Iron, %	Lead, %
1	65.22	34.76	0.01	0.01
2	70.61	29.33	0.02	0.04
3	75.37	24.56	0.05	0.02
4	79.96	20.02	0.01	0.005
5	85.22	14.76	0.01	0.005
6	90.01	9.97	0.01	0.01
7	94.26	5.67	0.05	0.02
8	97.19	2.75	0.05	0.01

Table III. Repeat Sparkings on Sample Containing 79.96% Copper

Run No.	1	2	3	4	5	6	7	8
$\dfrac{I\ 2884.4}{I\ 2882.9}$	0.60	0.62	0.62	0.60	0.60	0.61	0.61	0.59

Table IV. Spectrochemical Determination of Copper

	Copper Found %	Mean Value %	Av. Deviation from Mean %	Av. Deviation from Chemical Value %
Sample I 70.6% Cu, 0.75% Sn, remainder Zn	71.3, 71.1, 70.0, 69.4, 71.1, 70.2, 71.3, 71.0	70.7	0.60	0.63
Sample II 91.1% Cu, remainder Ni	91.1, 90.6, 90.7, 91.1, 88.3, 88.6, 91.4, 93.5	90.7	1.1	1.3
Sample III 94.6% Cu, remainder Ni	92.9, 94.0, 93.2, 92.5, 94.7, 94.3, 95.7, 93.3	93.8	0.86	1.1
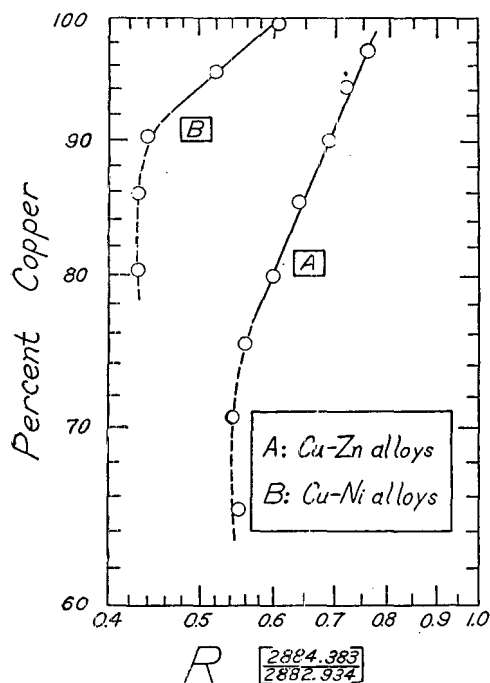
Figure 1. Working Curves for Determination of Copper

An example of the reproducibility of the intensity ratio is given in Table III.

A series of copper-nickel alloys was made by melting together C.P. metals in a graphite crucible in an induction furnace. The samples were cast as rods 6 mm. in diameter and about 12.5 cm. (5 inches) long. The ends were ground flat. They were analyzed chemically for copper only.

When above experiments were repeated with this series of alloys, the same effect was observed but only down to 85% copper. With lower percentages the intensity ratio remains essentially constant (curve B, Figure 1).

In Figure 1, the working curve for the copper-zinc and the copper-nickel alloys do not approach one another as the percentage of copper approaches 100%. That this is due, partly at least, to the difference in shape of the electrode is shown by the following experiment:

A piece of copper-zinc alloy, said by the supplier to contain 90% copper, in the form of 0.5-inch square column, was machined

down over half its length to a rod $^5/_{16}$ inch in diameter. The end of the rod and the flat surface of the other end were then sparked in the usual way. The intensity ratio of the 2884.4 Å. Cu II line to the 2882.9 Å. Cu I line was 0.67 for the flat surface and only 0.50 for the rod end. The square cross-section portion was then machined into cylindrical form, successively $^7/_{16}$, $^6/_{16}$, $^4/_{16}$, and $^7/_{32}$ inch in diameter. The intensity ratios were 0.57, 0.52, 0.42, and 0.40, respectively. Thus, in this method of analysis, it is absolutely essential that all the samples, both standard and unknown, be of the same size and shape.

As a test of the procedure, three samples of commercial alloys, similar to the standards in size and shape, were analyzed spectrographically with eight repeat runs (Table IV).

In order to determine the importance of the conditions of excitation, the copper-zinc alloys were rerun with Multisource settings $C = 5\mu f.$, $L = 100\mu h.$, and $R = 10r.$, which give a critically damped discharge rather than an oscillating one as was used above. Under these conditions, with the upper electrode positive, the intensity ratio of the 2884.4 Å. Cu II line to the 2882.9 Å. Cu I line remained constant over the entire percentage range.

DISCUSSION

A possible reason for this variation in the intensity ratio of the 2884.4 Å. Cu II line to the 2882.9 Å. Cu I line may be found in the variation in the thermal conductivity of the alloys. The thermal conductivity decreases with percentage of zinc up to about 32% zinc, where it goes through a minimum, while with copper-nickel alloys, it decreases with percentage of nickel to about 22% nickel and then remains constant over a long range. By reference to Figure 1, we see that the intensity ratio of the 2884.4 Å. Cu II to the 2882.9 Å. Cu I line decreases with percentage of zinc down to about 30% zinc, where it goes through a minimum, while it decreases with percentage of nickel down to about 15% nickel and then remains constant. Thus the variation of the intensity ratio is remarkably like that of the thermal conductivity. It seems probable that the lower the thermal conductivity, the less the heat conducted away and the more the energy available to vaporize the sample. Thus the discharge becomes more arclike and the intensity of the 2884.4 Å. spark line is decreased relative to the 2882.9 Å. arc line. This reasoning is further supported by the fact that the higher the percentage copper, and therefore the higher the thermal conductivity, the longer the exposure time required for a given intensity of the 2882.9 Å. Cu I line. To test further this assumption, a study of copper-tin alloys is planned.

These working curves, based on two lines of the same element, shift as is common for such curves obtained by the internal standard method. No reason for this was found. The work was done in an air-conditioned laboratory, but the humidity was not controlled.

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Procedure for Measurement of P^{31} and P^{32} in Plant Material

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A routine quantitative procedure for determining the specific activity of plant material containing radioactive phosphorus has been successfully applied to vegetative samples from greenhouse and field experiments. By comparison of the specific activity of the fertilizer preparation with that of the plants grown on soil receiving this fertilizer, the proportion of the phosphorus contained in the plants derived from the fertilizer may be estimated.

THIS paper considers in detail a routine quantitative procedure for determining the specific activity [P^{32}/(P^{31} + P^{32})] of plant material containing radioactive phosphorus. It has been successfully applied to a large number of vegetative samples from greenhouse and field experiments designed to study the utilization of phosphorus from fertilizers labeled with P^{32}. A comparison of the specific activity of the fertilizer preparation with that of the plants grown on a soil receiving this fertilizer enables estimation of the proportion of the phosphorus contained in the plants derived from this fertilizer. A considerable degree of precision (about 2 or 3%) in the measurement of the specific activity is a highly desirable prerequisite for experiments of this type.

In initial studies, the specific activities were calculated from direct measurements of the β-ray activity, with Geiger-Müller counters, of solutions prepared from plant material digested with nitric and perchloric acids. However, the sensitivity and accuracy of such a procedure did not prove satisfactory. Consequently, a method was worked out for precipitation of the phosphorus and its collection in a uniform manner prior to the radioactive measurement. The methods previously suggested for determining S^{35} (*3*) and 90-day arsenic (*4*) were helpful guides.
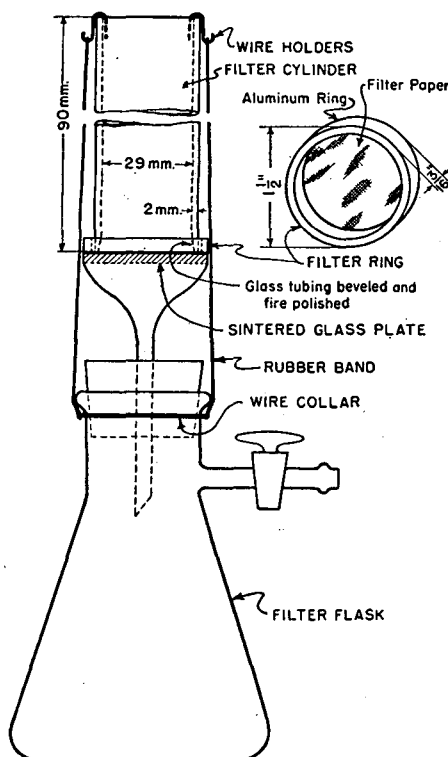
Figure 1. Filtration Apparatus for Collecting a Uniform Layer of Precipitate for Measurement of P^{31} and P^{32}

PROCEDURE

Samples of plant material containing from 5 to 30 mg. of P^{31} are digested with nitric and perchloric acids to destroy the organic matter and dehydrate the silica. After the silica is filtered off the phosphorus is precipitated as ammonium phosphomolybdate and then reprecipitated as magnesium ammonium phosphate. This precipitate is collected as a thin uniform layer on a filter ring under carefully standardized conditions, dried by washing with alcohol and ether, and finally stored in a desiccator at 50% relative humidity. The weight of this magnesium ammonium phosphate hexahydrate precipitate affords an estimation of the P^{31} and the radioactive measurement gives a value for the P^{32}.

FILTRATION APPARATUS

The filter rings (Figure 1) are prepared by cementing Whatman 42 filter paper to an aluminum ring. (The 3-M trim cement manufactured by Minnesota Mining & Manufacturing Co., Adhesive Division, 411 Piquette Ave., Detroit 2, Mich., was found very satisfactory for this purpose.) These rings are $^{3}/_{16}$-inch sections of seamless aluminum tubing 1.5 inches in outside diameter and with $^{1}/_{16}$ inch walls. Prior to use the filters are brought to equilibrium at 50% relative humidity (by placing in a desiccator containing sulfuric acid, specific gravity 1.33) and weighed.

The assembly of the filtration apparatus is shown in Figure 1. The filter ring is centered on a relatively fine sintered-glass suction plate and the glass cylinder is fitted in place and held tightly against the filter paper. Three rubber bands attached to a wire collar around the neck of the filter flask suffice to hold the cylinder in place. The inside edge of the glass cylinder pressing against the filter paper is beveled and fire-polished. The cylinder can then be removed without serious disturbance to the layer of the precipitate.

In handling the filter rings it is important to prevent wrinkling of the filter paper due to its expansion when wetted with water. If the filter paper is moistened with alcohol prior to placing the rings on the sintered-glass filter plate and if reduced pressure is maintained on the paper throughout the filtering process, no wrinkling will occur.

FILTRATION

It is necessary to exercise some care during the filtration of the magnesium ammonium phosphate to obtain the desired uniform layer of precipitate. Satisfactory results are obtained by the following procedure:

A filter ring is saturated with alcohol and centered on the sintered-glass filter plate and gentle suction is applied by adjusting the stopcock attached to the filter flask. The assembly of the apparatus is then completed and the supernatant liquid decanted into the filter with a minimum of disturbance to the precipitate. The walls of the beaker are washed with about 10 ml. of *N* ammonium hydroxide and the precipitate is rapidly transferred to the filter in one operation. This almost fills the cylinder with a suspension of the precipitate. The stopcock is then closed, thus retarding the filtration rate. The beaker is rapidly policed and washed. These washings are added to the filter cylinder before all the previous washings have had an opportunity to drain from the filter. Next, the stopcock is again opened and the filter allowed to drain. The walls of the filter cylinder are then policed and washed with 15 ml. of 50% alcohol by directing a fine stream around the top of the filter cylinder. This is followed by three washings with 95% alcohol. Finally, the filter is washed with 15 ml. of ether and air is drawn through the layer of precipitate for about 10 minutes or until dry. During the washing of the filter and precipitate care should be taken not to disturb the precipitate.

After the filtration is completed the rubber bands holding the cylinder are disconnected and the cylinder is carefully raised. Any particles adhering to the lower edges are recovered with a fine brush. The suction is then cut off, and the filter ring is removed and stored in a desiccator at 50% relative humidity for at least 12 hours before weighing.

Table I. Recovery of Phosphorus Weighed on Filter Rings as Magnesium Ammonium Phosphate Hexahydrate

Phosphorus Taken Mg.	$MgNH_4PO_4.6H_2O$ Recovered Mg.	Phosphorus Recovered Mg.
5	40.6	5.12
5	39.8	5.02
5	40.5	5.11
10	80.2	10.12
10	79.1	9.98
10	79.1	9.98
15	119.2	15.04
15	119.2	15.04
15	119.4	15.07

TYPICAL MEASUREMENTS

The weighing of magnesium ammonium phosphate hexahydrate as a procedure for determining phosphorus is not a commonly accepted practice. However, it has been recommended by Fales (2) and Treadwell and Hall (5). The results given in Table I show the recovery of phosphorus when weighed on filter rings as magnesium ammonium phosphate hexahydrate to be approximately equal to the phosphorus taken and to vary in direct proportion with the amounts taken.

The radioactivity measurements of the filter rings containing a layer of magnesium ammonium phosphate hexahydrate with a Geiger-Müller counter should not present difficulties if an arrangement for adequately reproducing the geometry is provided. A shield and sample holder similar to that described by Dauben et al. (1) has been in use at this laboratory. Self-absorp-

Table II. Radioactivity Measurements of Magnesium Ammonium Phosphate Precipitates Containing Varying Amounts of P^{31} and P^{32}

Relative P^{32} Concentration Taken	P^{31} Taken, Mg.	Activity^a, Counts/Sec.
1	10	8.01
	20	8.44
	30	8.21
2	10	15.70
	20	15.95
	30	16.01
3	10	23.80
	20	23.76
	30	24.02

^{a} Activity corrected for background, radioactive decay, and recovery time of counter.

tion was tested on amounts of precipitate up to 300 mg. and, as was expected, no correction appears necessary. Table II gives the radioactivity measurements of nine precipitates prepared to contain three amounts of P^{32} in combination with three amounts of P^{31}. The data show that the radioactivity of given amounts of P^{32} can be determined with accuracy in the presence of varying quantities of P^{31}. These data are representative of the degree of reproduction that has been obtained.

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Precipitation of Oxalates from Homogeneous Solution

Application to Separation and Volumetric Determination of Magnesium

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THE separation or determination of certain metals by precipitation with oxalate ion is an old but useful technique. A difficulty frequently encountered in such separations or determinations is the formation of finely divided precipitates that require retentive filter media. As a consequence filtration and washing may become slow and tedious operations. Though this manipulative difficulty may usually be overcome to a large extent by the familiar technique of adding the precipitant slowly and digesting the precipitated solution for a sufficiently long time, this does not always resolve the difficulty. When an oxalate is precipitated by such technique in a medium that is essentially nonaqueous, as in the method for the determination of magnesium described by Elving and Caley (1), the precipitate is still too finely divided and causes difficulty in filtration. What is needed therefore is a fundamentally different technique which will always result in the formation of an oxalate precipitate of large particle size that may be filtered and washed with ease and rapidity.

For the special case of the precipitation of calcium as oxalate, Willard and Chan (2) devised a procedure that produces a coarse precipitate that is easily filtered and washed. In this procedure part of the necessary oxalate is added to a calcium solution of such acidity that little or no initial precipitation results. Urea is then added and the solution is boiled gently to cause slow hy-

drolysis of the urea. This brings about gradual decrease in the hydrogen-ion concentration and a corresponding gradual increase in the oxalate-ion concentration, which in turn causes the slow precipitation of calcium oxalate in coarse crystals. The remainder of the necessary oxalate is then added to ensure complete precipitation. For the separation of thorium and most of the rare earths from a solution of a monazite sand, Willard and Gordon (3) found that the hydrolysis of methyl oxalate was a means of producing a slow increase in the concentration of oxalate ion, and that this technique yielded a precipitate of the mixed oxalates which was of better physical form than that obtained by the usual direct precipitation with oxalic acid.

Neither of these techniques for precipitation from homogeneous solution can be applied directly to the quantitative precipitation of certain other metal oxalates, such as the precipitation of magnesium oxalate in 85% acetic acid solution for example, though the principle involved in the second one appears to be generally applicable. In actual experiments on the use of methyl oxalate for the precipitation of magnesium oxalate in 85% acetic acid solution it was found that this ester decomposed too rapidly, especially at the elevated temperature desirable in this precipitation for the purpose of obtaining the best possible separation from lithium and sodium. However, the resulting precipitate was

Magnesium oxalate may be quantitatively precipitated in a dense and coarsely crystalline form from 85% acetic acid solution by the gradual release of oxalate ion in this medium as the result of the slow decomposition of dissolved ethyl oxalate. In contrast to a precipitate obtained by the direct addition of oxalate ion, one obtained by this technique may be filtered off and washed rapidly. By the use of this special technique of precipitation, the indirect method for the determination of magnesium based upon the solution of magnesium oxalate in dilute sulfuric acid and titration of the released oxalic acid becomes a very convenient and simple procedure.

noticeably superior to that produced by the procedure of Elving and Caley, though not markedly so. Evidently what was needed was a more stable, and yet sufficiently soluble, ester of oxalic acid that would decompose slowly in 85% acetic acid solution at an elevated temperature so as to bring about a much more gradual increase in oxalate-ion concentration.

After various preliminary experiments, ethyl oxalate was selected as the reagent that gave the best results under the optimum conditions for the precipitation of magnesium oxalate in this solution. These conditions are (1) the highest possible temperature that can be employed without danger of loss from bumping as the dense precipitate settles on the bottom of the precipitating vessel, and (2) a period of time for the formation of the precipitate of about 2 hours, as this yields a precipitate of very satisfactory character within a convenient working period. The precipitate of magnesium oxalate formed by this reagent under these conditions is strikingly different in physical character from that obtained by the precipitation procedure of Elving and Caley. Instead of being finely divided and voluminous it is coarsely crystalline and dense, and yet it does not adhere to the glass wall of the containing vessel as do some precipitates formed from homogeneous solution. This method of precipitation removes a principal objection to the analytical methods described by Elving and Caley, as the precipitate of magnesium oxalate may be very quickly filtered and washed. These workers found it impracticable to use a filter crucible because it became clogged with precipitate, and for this reason they were forced to use centrifugal separation and washing for their otherwise convenient volumetric method. The precipitate of magnesium oxalate formed by the present method may be rapidly filtered off on a glass or porcelain filter crucible of medium porosity. By thus eliminating the need for centrifugal separation, the volumetric method of Elving and Caley may be made the basis of an accurate and relatively rapid method for the determination of magnesium that requires no special equipment.

The production of oxalate ion by the hydrolysis of ethyl oxalate in 85% acetic acid is accompanied by a corresponding increase in hydrogen-ion activity, and unless some method of compensating for this is employed the solubility of magnesium oxalate in this medium is so increased that precipitation is not quantitative. The addition of a sufficient quantity of ammonium acetate is a convenient and satisfactory method of automatically controlling the hydrogen-ion activity within the necessary limits.

COMPOSITION OF THE PRECIPITATE

Elving and Caley did not investigate the composition of the precipitate formed in 85% acetic acid solution. In the course of investigating the possibility of determining magnesium gravimetrically by collecting, drying, and weighing the precipitated magnesium oxalate in a filter crucible, a number of experiments were made on the composition of the precipitate formed in this medium. It might be expected that the precipitate formed at high temperature in 85% acetic acid would be anhydrous, or at least contain considerably less water than the dihydrate precipitated from aqueous solution. Actually, the dihydrate is also

the salt precipitated from 85% acetic acid solution. However, as shown by the data in Table I, the composition of actual analytical precipitates does not correspond exactly to the theoretical composition of this salt. These precipitates were obtained by the quantitative precipitation of solutions of distilled magnesium (99.99% purity) by the procedure given below, and were dried to constant weight at 105° C. The magnesium content in terms of percentage was calculated from the magnesium taken and the weight of dried precipitate. This was found to be a more accurate procedure than analytical determination of the magnesium content of the precipitates by ignition to oxide and weighing. The oxalate content was determined by titration with permanganate; all the usual precautions were taken to secure high accuracy.

Table I. Experiments on Composition of Precipitates

Precipitate No.	Mg, %	C_2O_4, %	Mg/C_2O Ratio	MgC_2O, %
I	16.20	58.55	1.001	74.75
II	16.22	58.66	1.001	74.88
III	16.23	58.63	1.002	74.86
IV	16.29	58.83	1.002	75.12
Av.	16.23	58.67		74.90
Calcd. for $MgC_2O_4.2H_2O$	16.39	59.32		75.61

The ratio of magnesium content to oxalate content is close to theoretical, but the magnesium content, the oxalate content, and consequently the magnesium oxalate content fall appreciably below the theoretical. In other words, dried precipitates weigh more than they should, and high results may be expected in the gravimetric determination of magnesium on weighing such precipitates. In four trials on amounts of magnesium in the neighborhood of 50 mg., the results ranged from 0.3 to 0.6 mg. too high in terms of this element. Results sufficiently accurate for some purposes may, however, be obtained by this simple gravimetric method. The experiments indicated that the extra weight in such dried precipitates is due to small amounts of foreign substances adsorbed on or occluded in the precipitates when they are formed, and not removable by washing. For example, in an experiment where perchloric acid was used in the preparation of the magnesium sample, the almost indispensable procedure in actual practice, perchlorate ion was apparently present in the thoroughly washed precipitate, as was indicated by the presence of chloride ion in a nitric acid solution of the magnesium oxide obtained by ignition of the dried magnesium oxalate. It is likely also that the precipitates contain small amounts of occluded solvent not removable at a safe temperature for drying the hydrated magnesium oxalate.

The precipitate of magnesium oxalate obtained by this method may be ignited to magnesium oxide for weighing, but the time and trouble involved in this ignition, and the lower accuracy often obtained in practice, make this gravimetric method less desirable than the volumetric. Because of the voluminous nature of the precipitate obtained by their method of precipitation, Elving and Caley found that 25 mg. was the highest amount of magnesium that could conveniently be determined volumetrically, but this limitation is now removed and 100 mg. or even more can be determined by the present method of precipitation. In other words,

there is now no good reason to prefer the gravimetric method to the volumetric, and hence only the volumetric method is here described and recommended.

PROCEDURE

Concentrate the neutral magnesium solution contained in a 250-ml. beaker to a volume of 14 to 15 ml., or dissolve the residue of dried salts containing the magnesium in sufficient water to reach this same volume. Add 75 ml. of glacial acetic acid and stir until solution is complete. Then add 10 ml. of glacial acetic acid containing 1 gram of ammonium acetate. Finally add 1.5 ml. of ethyl oxalate and stir thoroughly. Cover the beaker with a watch glass and place it on an electric hot plate so regulated that the solution may be raised to approximately 100° C. and held at this temperature. From the time precipitation begins, heat for 2 hours if the amount of magnesium is 50 mg. or less, and for 3 hours if the amount of magnesium is as high as 100 mg. As a precautionary measure, especially if there is doubt as to the full maintenance of the proper temperature throughout the period of precipitation, add, 15 minutes before filtration, 5 ml. of 85% acetic acid that has been saturated with ammonium oxalate at room temperature.

Filter while hot through a glass or porcelain filter crucible of medium porosity. Remove the precipitate from the beaker with the aid of a rubber-tipped stirring rod and warm (70° to 80° C.) 85% acetic acid, preferably delivered from an all-glass, bulb-operated wash bottle. After transferring all of it to the crucible, wash the precipitate with four or five additional portions of warm acid of about 5 ml. each. Rinse out the suction flask thoroughly with distilled water and after replacing the empty flask dissolve the precipitate and wash out the crucible with successive portions of warm (80° C.) 5% sulfuric acid until a total of 200 ml. has collected in the suction flask. Titrate this solution at once with permanganate solution that has been standardized against sodium oxalate at a titration temperature of 70° to 80° C.

Notes on the Procedure. Inasmuch as each milliliter of a 0.1000 N permanganate solution is equivalent to only 0.001216 gram of magnesium it is desirable, in order to avoid the inconvenience of refilling the buret, to take a sample of such size that not more than 50 to 55 mg. of magnesium are present when an ordinary buret and permanganate solution of the usual concentration are used. For larger amounts the use of a 100-ml. buret or a more concentrated permanganate solution is a convenience.

The substances that interfere in this procedure are essentially those listed by Elving and Caley. However, sulfate interferes more in this procedure than in theirs, and oxalate must be entirely absent. In adapting the present method to the general quantitative scheme the practical procedure after separation of calcium as oxalate is to remove ammonium salts and oxalate completely by treatment with nitric and perchloric acids, and to fume off the excess of perchloric acid, so that there is finally obtained a dry neutral residue of the perchlorates of magnesium and the alkali metals which is then dissolved in the recommended volume of water.

Instead of first adding the 75 ml. of glacial acetic acid and then the 10 ml. of the 10% solution of ammonium acetate in glacial

acetic acid it is equally satisfactory, and perhaps more convenient, to add at once 85 ml. of glacial acetic acid in which has been dissolved 1 gram of ammonium acetate.

It is essential that the ethyl oxalate be pure diethyl oxalate and that it contain no ethyl hydrogen oxalate such as is formed by contact of diethyl oxalate with water or moist air. This reagent as purchased from the usual commercial sources has been found to be of satisfactory quality. However, when pure diethyl oxalate is allowed to stand in a partly filled container that is opened frequently in humid weather sufficient hydrolysis takes place to render the reagent unfit for use. The partly hydrolyzed ester decomposes too rapidly and causes the formation of a fine precipitate.

Instead of using a filter crucible and a suction flask for the filtration it is also feasible to use a filter stick, though for work on the macro scale this technique is not advantageous.

TEST ANALYSES

The results of a series of test analyses on pure magnesium solutions, prepared from vacuum-distilled magnesium of 99.99% purity, are shown in Table II. Essentially the same results were obtained on both types of solutions tried and the difference errors were small and of practically the same magnitude regardless of the amount of magnesium determined. In Table III are shown the results of a similar series of test analyses in which magnesium was determined in the presence of varying amounts of lithium. The results are generally satisfactory, although there is a definite tendency toward high results, especially in certain ranges.

Elving and Caley found that of all the alkali metals lithium interferes most in this general method. However, a comparison of the present results with those obtained by Elving and Caley shows that the interference from lithium is less by the present procedure than by their procedure. It is likely that there is less coprecipitation of lithium oxalate by the present procedure, both because of the slower rate of precipitation and because of the larger particle size with correspondingly less total surface. By using the present procedure for the determination of magnesium in the presence of lithium double precipitation is less often a necessity. Test analyses on the determination of magnesium in the presence of sodium showed that there is little interference

Table II. Determination of Magnesium Alone

Anion Present	Mg Taken	Mg Found	Difference, Error
	Gram	Gram	Gram
Chloride	0.0011	0.0010	−0.0001
	0.0011	0.0009	−0.0002
Perchlorate	0.0010	0.0011	+0.0001
	0.0010	0.0010	±0.0000
Chloride	0.0112	0.0111	−0.0001
Perchlorate	0.0112	0.0113	+0.0001
Chloride	0.0224	0.0225	+0.0001
	0.0224	0.0224	±0.0000
Perchlorate	0.0224	0.0227	+0.0003
	0.0202	0.0203	+0.0001
Chloride	0.0505	0.0506	+0.0001
	0.0563	0.0561	−0.0002
	0.0563	0.0562	−0.0001
Perchlorate	0.0563	0.0562	−0.0001
	0.0563	0.0562	−0.0001
	0.0563	0.0562	−0.0001
Chloride	0.1010	0.1008	−0.0002
Perchlorate	0.1010	0.1008	−0.0002

Table III. Determination of Magnesium in the Presence of Lithium

Anion Present	Li Present	Mg Taken	Mg Found	Difference, Error
	Gram	Gram	Gram	Gram
Chloride	0.010	0.0112	0.0115	+0.0003
Perchlorate	0.010	0.0101	0.0103	+0.0002
Chloride	0.010	0.0505	0.0507	+0.0002
	0.010	0.0505	0.0507	+0.0002
	0.010	0.1010	0.1010	±0.0000
Perchlorate	0.010	0.1010	0.1012	+0.0002
Perchlorate	0.020	0.0563	0.0564	+0.0001
	0.020	0.0563	0.0565	+0.0002
	0.040	0.0563	0.0565	+0.0002
	0.040	0.0563	0.0567	+0.0004
	0.070	0.0505	0.0509	+0.0004
	0.070	0.0505	0.0510	+0.0005
Chloride	0.100	0.0011	0.0010	−0.0001
	0.100	0.0011	0.0009	−0.0002
	0.100	0.0112	0.0115	+0.0003
	0.100	0.0112	0.0115	+0.0003

Table IV. Determination of Magnesium in the Presence of Sodium

Anion Present	Na Present	Mg Taken	Mg Found	Difference Error
	Gram	Gram	Gram	Gram
Chloride	0.040	0.0505	0.0506	+0.0001
Perchlorate	0.040	0.0505	0.0507	+0.0002
Chloride	0.100	0.0101	0.0102	+0.0001
Perchlorate	0.100	0.0101	0.0103	+0.0002
Chloride	0.100	0.0505	0.0507	+0.0002
Perchlorate	0.100	0.0505	0.0507	+0.0002

from moderate amounts of sodium, as is indicated by a few typical results given in Table IV. In ordinary cases double precipitation is not necessary when this procedure is used.

In view of the prior experiments of Elving and Caley on the determination of magnesium in samples of actual materials by this general method, it seemed unnecessary to run test analyses by this special precipitation procedure on such materials.

Preliminary experiments have shown that the slow hydrolysis of esters of oxalic acid may be applied in a similar way to the precipitation of the oxalates of zinc, cadmium, and lead in an easily filterable state for the purpose of their quantitative determination.

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Analysis of Simple and Complex Tungsten Carbides

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Methods for separating and estimating the principal constituents of tungsten carbides are described. Tungsten is precipitated with cinchonine and α-benzoinoxime after decomposition of sample by fusion with sodium peroxide. Columbium, tantalum, titanium, and iron are separated from tungsten and molybdenum by precipitation with sodium and ammonium hydroxides; and columbium and tantalum are separated from iron and the bulk of titanium by hydrolysis. Columbium and tantalum are precipitated with cupferron; also titanium after separation from iron by hydrogen sulfide. Cobalt and nickel are determined electrometrically after separation from interfering elements with potassium hydroxide. After separation from tungsten and molybdenum with ammonium hydroxide, chromium is determined by ammonium persulfate method. Manganese is determined colorimetrically with potassium periodate after separations involving potassium hydroxide and hydrolysis. Sodium peroxide fusion, followed by dehydration with perchloric acid and purification with sodium pyrosulfate–sulfuric acid, separates silicon, and carbon is determined by combustion in oxygen.

THE analysis of tungsten carbide containing tungsten, molybdenum, cobalt, nickel, columbium, tantalum, titanium, chromium, iron, silicon, manganese, and carbon is time-consuming and tedious, and good technique is essential if accurate results are to be obtained. The literature on the analysis of complex tungsten carbides is limited and leaves much to be desired as regards the solution of the difficulties encountered in the analysis of these materials. By the procedures described hereinafter, interfering elements are either removed or determined and proper corrections are made. An analysis for the elements mentioned may be made in about 2.5 days.

The fusion method for tungsten involves fusion of the alloy with sodium peroxide in a nickel crucible, solution in hydrochloric acid, and addition of cinchonine (or cinchonine-antipyrine) and α-benzoinoxime to ensure the complete precipitation of the tungsten and molybdenum, followed by filtration, ignition, and weighing. The precipitate is tested colorimetrically for molybdenum, and for columbium, tantalum, and titanium by precipitation with cupferron in the presence of tartrate ion to ensure complete separation from tungsten. A solution method for tungsten involves dissolving the sample in hydrofluoric and nitric acids in platinum, and evaporating to a low volume, followed by transferring the solution to a beaker containing boric acid, adding hydrochloric and nitric acids, evaporating, and completing the determination for tungsten as for the fusion method.

In the method for columbium, tantalum, titanium, and iron, the tungsten and molybdenum are removed by precipitation with a very small excess of ammonium hydroxide and filtration after the sulfuric acid solution of the sample has been treated with an excess of sodium hydroxide solution (200 grams per liter), boiled, and acidified with hydrochloric acid. The ammonium hydroxide precipitate is treated with nitric and perchloric acids, the solution is evaporated to dense fumes of perchloric acid, and columbium and tantalum are hydrolyzed by boiling with dilute hydrochloric and sulfurous acids, and separated from the iron and the greater part of the titanium by filtration. The last traces of tungsten are removed from the columbium and tantalum by precipitation with cupferron in the presence of tartaric acid. The iron is separated from the bulk of the titanium by precipitation with ammonium sulfide in the presence of ammonium tartrate and completed by titration with potassium dichromate. The titanium in the ammonium sulfide filtrate is recovered by precipitation with cupferron.

Cobalt and nickel are determined electrolytically after the tungsten and molybdenum and the bulk of the tantalum and columbium have been removed by a double precipitation with potassium hydroxide and filtration. Cobalt is also determined potentiometrically after a similar precipitation with potassium hydroxide and filtration.

The method for chromium consists in removing the tungsten and molybdenum by treatment of the sulfuric acid solution of the sample with ammonium hydroxide and filtration, the destruction of the precipitate with nitric and perchloric acids, and the completion of the determination by the ammonium persulfate method.

In the determination of manganese, the tungsten and molybdenum and the bulk of the columbium and tantalum are removed by treatment of the sulfuric acid solution with potassium hydroxide and filtration. The remaining columbium and tantalum are separated by hydrolysis and filtration, and the manganese in the filtrate is determined colorimetrically by the potassium periodate method.

Silicon is determined by fusion of the sample with sodium peroxide, dehydration with perchloric acid, separation from tungstic, columbic, and tantalic acids by fusion with sodium pyrosulfate, and treatment of the sodium pyrosulfate–sulfuric acid solution with diluted tartaric acid, followed by filtration and washing.

Carbon is determined by combustion with ingot iron and cupric oxide, and the resulting carbon dioxide is absorbed in Ascarite and weighed.

RECOMMENDED PROCEDURES FOR TUNGSTEN

Tungsten I. Mix 1.0000 gram of the 80- to 100-mesh sample (prepared in a tungsten carbide mortar equipped with a pestle also made of tungsten carbide) with 10 grams of dry sodium peroxide (weighed on a rough balance) in a 50-ml. nickel crucible, and cover with a layer of 1 to 2 grams of sodium peroxide. Fuse carefully by revolving the crucible in the outer edge of the flame of a laboratory burner at a temperature of 700° to 800° C. until the entire mass has blackened; as the mixture begins to fuse, rotate the crucible vigorously to keep the heavy particles of the sample in suspension, and increase the temperature to approximately 900° C. for 4 or 5 minutes. It is important that the sample be decomposed at this point, as there is no opportunity later on to treat any undecomposed residue.

Allow the crucible to cool almost to room temperature, cover, and tap on a solid object to loosen the melt. Transfer the cake to a dry 800-ml. covered beaker, and add 65 ml. of concentrated hydrochloric acid all at once. Rinse the crucible first with 10 ml. of hydrochloric acid (1 to 1), then with about 25 ml. of hot water, and add the rinsings to the beaker. Add from 25 to 50 ml. of warm water, boil for 3 or 4 minutes to dissolve nickel oxide extracted from the crucible, and dilute to 400 ml. with boiling water. Add 5 ml. of cinchonine solution or 20 ml. of the cinchonine-antipyrine solution, boil for from 3 to 5 minutes, and cool to 15° C. in cold water. Add a little ashless paper pulp and 5 ml. (or a sufficient amount to precipitate any molybdenum and tungsten in solution) of a 3% acetone solution of α-benzoinoxime, and stir vigorously for several minutes; filter through an 11-cm. paper containing a little ashless paper pulp, and wash at least 15 times with cold wash solution A or B.

Transfer the paper and precipitate to the original 800-ml. beaker, add 40 ml. of hydrochloric acid (1 to 1), macerate the paper to a pulp with a glass rod, and digest for 3 to 5 minutes at a temperature of 80° to 90° C. Add 3 ml. of concentrated nitric acid and continue the heating for several minutes longer. Dilute to 400 ml. with boiling water, add 5 ml. of cinchonine solution or 20 ml. of the cinchonine-antipyrine solution, boil for from 3 to 5 minutes, and cool to 15° C. in cold water. Repeat the addition of 5 ml. of the 3% acetone solution of α-benzoinoxime, stirring, filtering, and washing as previously described. The filtration is preferably made by suction. Ignite the paper and precipitate in a weighed 50- or 100-ml. platinum dish at a temperature of 500° to 600° C. to burn off the paper, cool, add from 1 to 2 ml. of hydrofluoric acid, 1 ml. of nitric acid, and 0.5 ml. of sulfuric acid (1 to 1), and evaporate to dryness on a sand bath. Again ignite for a few minutes at approximately 600° C., and then for 30 minutes (to constant weight) at 750° to 800° C., cool, and weigh.

Dissolve the ignited and weighed tungsten and molybdenum oxide precipitate in 50 ml. or more of hot sodium hydroxide solution (200 grams per liter), transfer to a 250-ml. beaker with approximately 75 ml. of hot water, and boil for several minutes to dissolve the tungsten. Cool, make the solution slightly acid with sulfuric acid (1 to 1), then add a slight excess of ammonium hydroxide, and boil until only a very faint odor of ammonia remains. Filter through a 9-cm. paper containing a little ashless paper pulp, and wash from 12 to 15 times with ammonium sulfate solution (50 grams per liter) containing 1 or 2 drops of ammonium hydroxide per liter. Reserve the filtrate and test colorimetrically for molybdenum. Return the paper and precipitate to the beaker, add 50 ml. of hydrochloric acid (1 to 9), macerate the paper to a pulp, and heat to boiling. Add a few drops of bromocresol purple indicator and ammonium hydroxide (1 to 1) until the color just changes to a distinct purple. Boil for 1 minute, and filter and wash as before. Ignite in a 100-ml. platinum dish at a temperature of 500° to 600° C. to burn off the paper, cool, add 10 ml. of hydrofluoric acid, stir well with a platinum rod, heat to obtain a clear solution, and evaporate to 1 ml. on a hot water bath.

NOTE I. In case the alloy is high in tantalum, the ignited precipitate will be found more difficult to dissolve when treated with hydrofluoric acid, in which case the following treatment should be used:

Fuse the ignited precipitate with 3 to 5 grams of potassium pyrosulfate at a temperature of approximately 750° C. and dissolve the cold melt in 200 ml. of tartaric acid solution (100 grams per liter) at a temperature not exceeding 70° C. If the solution is permitted to boil, some tungsten may separate. Cool to 15° to 20° C., add a little ashless paper pulp, and precipitate any tantalum and columbium with cupferron as described. Filter through a 9-cm. paper containing a little ashless paper pulp, and wash 18 to 20 times with cold hydrochloric acid (1 to 9) containing 5 ml. of the cupferron reagent per liter; discard the filtrate. The precipitation of the columbium, tantalum, etc., with cupferron from a tartaric acid solution and filtration serves to remove any remaining tungsten.

Ignite the precipitate in a 50- or 100-ml. platinum dish at 500° to 600° C. to burn off the carbon of the filter paper, cool, add 10 ml. of hydrofluoric acid, and evaporate to 1 ml. on a steam bath. Add 25 ml. of tartaric acid solution (250 grams per liter), stir well, and heat for several minutes at a temperature of approximately 90° C. Add 25 ml. of boric acid solution (40 grams per liter), heat 5 to 10 minutes at approximately 90° C., transfer to a 250-ml. beaker, and rinse the platinum dish with five 5-ml. portions of hot tartaric acid solution (20 grams per liter). Cool to 15° to 20° C. and proceed with the cupferron precipitation, filtration, and ignition as described. The treatment with hydrofluoric acid, reprecipitation with cupferron, and filtration ensure the complete removal of all potassium salts.

Add 25 ml. of tartaric acid solution (250 grams per liter), stir well, and heat for several minutes at a temperature of approximately 90° C. Add 25 ml. of boric acid solution (40 grams per liter), heat from 5 to 10 minutes at approximately 90° C., transfer to a 250-ml. beaker, and rinse the platinum dish with five 5-ml. portions of hot tartaric acid solution (20 grams per liter). (Once the solution has been transferred to the 250-ml. beaker, the determination should be carried out promptly.) Cool to 15° to 20° C. and add a slight excess of a freshly prepared, filtered, cold 6% water solution of cupferron, and stir vigorously for several minutes. An excess of the reagent is indicated when one drop forms a snow-white precipitate that rapidly disappears. Add 1 to 2 ml. more of the reagent, stir well, filter through two superimposed 11-cm. papers (containing a little ashless paper pulp) supported on a platinum cone, employing moderate suction and wash at least 20 to 25 times with cold hydrochloric acid (1 to 9) that contains 5 ml. of the cupferron reagent per liter. Ignite in platinum first at a low temperature and finally for 30 minutes (to constant weight) at 750° to 800° C., cool, and weigh. The precipitation with cupferron in the tartaric acid solution and filtration as described serve to remove any tungsten remaining in the ammonia precipitate.

Add 20 ml. of tartaric acid solution (500 grams per liter) to the combined ammoniacal filtrates reserved for molybdenum, and make just acid with sulfuric acid (1 to 1). Add 10 ml. of ferric sulfate solution (80 grams per liter), and cool to 20° to 25° C. Add 5 ml. of sodium thiocyanate solution (100 grams per liter) and 10 ml. of stannous chloride solution (350 grams per liter), and then sufficient sulfuric acid (1 to 1) to give a solution containing sulfuric acid (1 to 9) by volume. Stir well, cool immediately to 25° C., and transfer to a 500-ml. separatory funnel, using from 50 to 75 ml. of isopropyl ether (ethyl or butyl acetate may be used in place of isopropyl ether); stopper the funnel, shake vigorously for from 3 to 5 minutes, and let stand until the liquids have separated into two distinct layers.

Draw off the lower or acid layer into the original beaker, and then the ethereal layer containing the molybdenum into a 100-ml. volumetric flask; rinse the funnel with a few milliliters of ether that has previously been prepared by shaking with 100 ml. of cold sulfuric acid (1 to 9) containing 0.8 gram of ferric sulfate, sodium thiocyanate, and stannous chloride as described above, drawing off the lower layer and discarding. Return the lower or acid layer from the original beaker to the funnel and shake with an additional 25 ml. of ether. Draw off the lower layer and

discard if not more than a trace of molybdenum is shown; otherwise, return it to the funnel and shake with an additional 10 ml. of ether. Add the ethereal layer to the main molybdenum solution in the 100-ml. flask, and dilute to the mark with ether that has been prepared as previously described. Complete the determination by visual reading of the color or preferably in a photoelectric colorimeter of the Fisher or similar type, using green filter No. 525. Each milliliter of the extracted solution should not contain more than 0.03 mg. of molybdenum per ml. Multiply the amount of molybdenum found by 1.5 to obtain the corresponding amount of molybdenum trioxide. Deduct the molybdenum trioxide found plus the weight of the ignited and weighed cupferron precipitate from the weight of impure tungsten trioxide, multiply the remainder by 79.3, and divide by the weight of sample taken to obtain the per cent tungsten.

Tungsten II. Transfer 0.5000 gram of the 80- to 100-mesh sample to a large platinum dish, add from 10 to 15 ml. of hydrofluoric acid and from 2 to 3 ml. of concentrated nitric acid, cover with a platinum lid, and heat at a temperature of approximately 90° C. until the reaction begins; continue the addition of nitric acid cautiously, with heating, until complete decomposition is obtained. Remove and rinse the cover with a little water and then rinse down the sides of the dish. Evaporate slowly until the volume is reduced to about 3 ml., or just before tungsten begins to separate. Transfer to a 600-ml. beaker containing 100 ml. of boric acid solution (40 grams per liter), and rinse the dish successively with hot water, 1 ml. of hot ammonium hydroxide, water, 2 ml. of hydrochloric acid, and finally with water. Add 20 ml. of hydrochloric acid and 5 ml. of concentrated nitric acid, and slowly evaporate to a volume of from 15 to 20 ml. Dilute to 350 ml. with hot water, add 5 ml. of cinchonine solution or 20 ml. of the cinchonine-antipyrine solution, boil for at least 3 minutes, cool to 15° C., and complete the determination as described under tungsten.

Solutions Required. CINCHONINE SOLUTION. Dissolve 125 grams of the reagent in 1 liter of hydrochloric acid (1 to 1).

CINCHONINE-ANTIPYRINE. Dissolve 10 grams of cinchonine in 40 ml. of hydrochloric acid (1 to 1), add to 960 ml. of water containing 40 grams of antipyrine, and stir well.

α-BENZOINOXIME SOLUTION. Dissolve 5 grams of the reagent in 95 ml. of c.p. acetone and 5 ml. of water, and filter. Store in a cool place and do not use if more than 5 days old.

WASH SOLUTION A (α-Benzoinoxime Solution). Add 2 ml. of the 5% acetone solution of α-benzoinoxime and 2 ml. of cinchonine solution to 1 liter of hydrochloric acid (2 to 98).

WASH SOLUTION B (α-Benzoinoxime–Antipyrine Solution). Add 2 ml. of the 5% acetone solution of α-benzoinoxime and 10 ml. of the cinchonine-antipyrine solution to 1 liter of hydrochloric acid (2 to 98).

FERRIC SULFATE SOLUTION (8%). Dissolve 80 grams of the salt in 1 liter of sulfuric acid (1 to 4).

STANNOUS CHLORIDE SOLUTION. Dissolve 350 grams of the salt in 200 ml. of hot hydrochloric acid (1 to 1), cool, and dilute to 1 liter.

BROMOCRESOL PURPLE INDICATOR. Dissolve 0.1 gram of the indicator in 9.25 ml. of 0.02 N sodium hydroxide solution and dilute to 200 ml. with cold distilled water.

COLUMBIUM, TANTALUM, AND TITANIUM

Transfer 0.5000 gram of the 80- to 100-mesh sample to a 100-ml. (or larger) platinum dish, add from 10 to 15 ml. of hydrofluoric acid and from 2 to 3 ml. of concentrated nitric acid, cover with a platinum lid, and heat at a temperature of approximately 90° C. for several minutes; continue the addition of nitric acid cautiously, with heating, until complete solution is obtained. Remove and rinse the cover with a little water, and then rinse down the sides of the dish. Cautiously add 20 ml. of concentrated sulfuric acid and evaporate on a sand bath to fumes of sulfur trioxide. Allow to cool somewhat, transfer to an 800-ml. beaker, and rinse the dish successively with warm water, hot sodium hydroxide solution (200 grams per liter) to remove adhering tungstic acid, hot water, hydrochloric acid, and finally with hot water. Dilute to approximately 300 ml. with hot

water, and heat to boiling. Cool, add a 20-ml. excess of sodium hydroxide solution (200 grams per liter), and boil for several minutes. Acidify with hydrochloric acid, add a slight excess of ammonium hydroxide, and boil until only a very faint odor of ammonia remains. Dilute to approximately 600 ml. with boiling water, stir well, allow the precipitate to settle, and filter through an 11-cm. paper containing a little ashless paper pulp. Wash 10 or 12 times with hot ammonium chloride solution (20 grams per liter) containing from 2 to 3 drops of ammonium hydroxide per liter.

Transfer the paper and precipitate to the original 800-ml. beaker, add 200 ml. of hot hydrochloric acid (1 to 9), macerate the paper to a pulp by means of a glass rod, and heat to boiling. Dilute to 400 ml. with boiling water, add a slight excess of ammonium hydroxide, and boil until only a very faint odor of ammonia remains. Filter through an 11- or 12.5-cm. paper containing a little ashless paper pulp, and wash from 12 to 15 times with hot ammonium chloride solution (20 grams per liter) containing 2 to 3 drops of ammonium hydroxide per liter; discard the filtrate. Transfer the paper and precipitate to a 400-ml. beaker, add 25 ml. of concentrated nitric acid and 15 ml. of perchloric acid (70%), evaporate to dense fumes of perchloric acid, and continue the fuming for at least 10 minutes longer; this length of fuming is very important, because by this hard fuming the columbium and tantalum oxides are completely precipitated and contain only a fraction of the titanium present. Cool, add 175 ml. of warm water, 10 ml. of concentrated hydrochloric acid, and approximately 50 ml. of sulfurous acid (6%), and boil for 5 minutes. Allow to stand for 30 minutes or until the supernatant liquid is clear, filter (preferably by suction) through an 11-cm. paper containing a little ashless paper pulp, and wash 18 or 20 times with hydrochloric acid (2 to 98); reserve the filtrate for titanium and iron.

Ignite in a 100-ml. platinum dish at a temperature of 500° to 600° C. (no higher) to burn off the paper, cool, add from 5 to 10 ml. of hydrofluoric acid, and evaporate the solution on a steam bath to a volume of 1 ml. If the oxides fail to dissolve completely, add an additional 10 ml. of hydrofluoric acid and repeat the evaporation to a volume of 1 ml. (In case of high tantalum material, the procedure outlined under Tungsten I, Note I, should be followed.) Remove from the heat, add 20 ml. of tartaric acid solution (500 grams per liter) and 25 ml. of boric acid solution (40 grams per liter). Cool to 15° to 20° C., transfer to a 250-ml. beaker, and rinse the dish well with cold water. Immediately dilute to 100 ml. with cold water, add a little ashless paper pulp, and precipitate the columbium, tantalum, and remaining titanium by the addition of a freshly prepared, filtered, cold 6% water solution of cupferron. An excess of the reagent is indicated when one drop forms a snow-white precipitate that rapidly disappears. Add 1 to 2 ml. more of the cupferron solution, stir well, and filter through an 11-cm. paper (containing a little ashless paper pulp) supported on a platinum cone, employing moderate suction; wash 20 to 25 times with cold hydrochloric acid (1 to 9) containing 5 ml. of the cupferron reagent per liter; discard the filtrate.

The small amount of hydrofluoric acid remaining and the tartaric acid used serve to hold up any small amount of tungsten present. Ignite in a weighed 100-ml. platinum dish at 500° to 600° C. to burn off the paper, and finally for 30 minutes (to constant weight) at 1000° to 1050° C., cool, and weigh. Fuse with from 3 to 5 grams of potassium pyrosulfate (or a sufficient amount to obtain a clear fusion) at a temperature of approximately 750° C., cool, add 20 ml. of concentrated sulfuric acid, and heat to obtain a clear solution. Cool somewhat, pour into a 250-ml. beaker (A) containing 50 ml. of cold distilled water and 1 ml. of hydrogen peroxide (30%), rinse the platinum dish with 50 ml. of water containing 1 ml. of hydrogen peroxide (30%), mix well, and cool to room temperature. To another 250-ml. beaker (B) add 100 ml. of water in which are dissolved the same

amount of potassium pyrosulfate as was used in making the fusion, 20 ml. of concentrated sulfuric acid, and 2 ml. of hydrogen peroxide (30%), mix well, and cool to room temperature. To beaker B add a measured amount of standard titanium sulfate solution from a buret, with stirring, until it contains slightly less titanium than the sample.

Equalize the volume of the standard and that of the sample by adding the necessary amount of cold sulfuric acid (1 to 4), then add equal additional volumes of the standard titanium sulfate solution and cold sulfuric acid (1 to 4) to the standard and sample, respectively. Mix, and compare the solutions after each addition until the colors of the two solutions match exactly. The solution should not contain more than 0.1 mg. of titanium per ml. Multiply the number of milliliters of the standard titanium sulfate solution used by 0.0005 to obtain the weight of titanium in the ignited cupferron precipitate. Multiply the weight of titanium found by 1.668 to obtain the corresponding weight of titanium dioxide.

Solutions Required. STANDARD TITANIUM SULFATE SOLUTION (1 ml. = 0.0005 gram of titanium). Fuse 1.7 grams of c.p. titanium dioxide in a large platinum dish with approximately 10 grams of potassium pyrosulfate, cool, and dissolve the melt in 200 ml. of sulfuric acid (1 to 9); transfer to a 2-liter flask, cool to room temperature, and dilute to the mark with cold sulfuric acid (1 to 9). Standardize this solution by heating a 100-ml. aliquot portion to 60° to 70° C., and passing it through a Jones zinc reductor [which has just been cleaned by passing 100 ml. of sulfuric acid (2 to 98) through it and discarding] into 30 ml. of ferric phosphate solution; follow with 100 ml. of hot (60° to 70° C.) sulfuric acid (2 to 98), and 50 ml. of water, add 1 to 2 drops of o-phenanthroline, and titrate with 0.1 N potassium permanganate to a green. During the passage of the solution, the tip end of the reductor tube should dip just beneath the surface of the solution in the suction flask. Run a blank by passing 100 ml. of hot concentrated sulfuric acid (1 to 9) and the same amount of wash solution through the reductor into 30 ml. of ferric phosphate solution, and titrating with 0.1 N potassium permanganate. One milliliter of 0.1 N potassium permanganate = 0.00479 gram of titanium.

FERRIC PHOSPHATE SOLUTION. Add 150 grams of ferric sulfate to 500 ml. of water, 150 ml. of phosphoric acid (85%), and 10 ml. of concentrated sulfuric acid, heat until dissolved, cool, and dilute to 1 liter. Add potassium permanganate solution (25 grams per liter) dropwise until the pink color persists for 30 seconds.

o-PHENANTHROLINE FERROUS ION INDICATOR. Dissolve 1.49 grams of the indicator in 100 ml. of cold water containing 0.7 gram of ferrous sulfate heptahydrate.

COLUMBIUM BY REDUCTION

After determining titanium by color comparison, add 0.0500 gram of pure titanium dioxide [which has been fused with approximately 3 grams of potassium pyrosulfate and dissolved in 50 ml. of sulfuric acid (1 to 4)] and 10 ml. of concentrated sulfuric acid, and dilute to 200 ml. with water; then add 2 grams of succinic acid, stir, and heat until dissolved. (The titanium solution added helps to prevent hydrolysis of the columbium and tantalum in the reductor.) Pass 100 ml. of hot sulfuric acid (heated to 60° to 70° C.) (1 to 4), the columbium and titanium solution, 150 ml. of hot sulfuric acid (1 to 4) containing 1 gram of dissolved succinic acid, and three 50-ml. portions of cold water, in the order named, through a 30-inch Jones reductor [which has just been cleaned with 100 ml. of sulfuric acid (3 to 97) and 200 ml. of nearly boiling water, the washings being discarded] into a 1-liter suction flask containing 25 ml. or more of ferric phosphate solution and 25 ml. of water, the tip of the reductor tube dipping just beneath the surface of this solution. Cool to room temperature, using ice cubes made from distilled water, if necessary. Add several drops of o-phenanthroline and titrate with 0.05 N potassium permanganate (1 ml. = 0.002323 gram of columbium or 0.003323 gram of columbium pentoxide and 0.002395 gram of titanium or 0.003995 gram of titanium dioxide) to a clear green color. The indicator changes from pink to clear green. The total time required to draw the columbium and wash solutions through the reductor should not be less than 10 minutes and preferably 12 minutes. At no time allow

the funnel which forms the top of the reductor to become entirely empty; when idle, the reductor should always be filled with distilled water to above the top of the zinc.

Run a blank by fusing 0.0500 gram of pure titanium dioxide with the same amount of potassium pyrosulfate as was used in fusing both the titanium dioxide and combined oxides, dissolve the melt in 200 ml. of sulfuric acid (1 to 4) containing 2 ml. of hydrogen peroxide (30%) and 2 grams of succinic acid, and heat until dissolved. Heat the solution to 60° to 70° C., pass through the reductor into 25 ml. of ferric phosphate solution as described, cool to room temperature, and titrate with 0.05 N potassium permanganate. The volume of 0.05 N potassium permanganate solution used, less the blank (including the titanium dioxide added), less the amount equivalent to the titanium in the combined oxides obtained by color comparison, multiplied by 0.003323, gives the weight of columbium pentoxide. The weight of total oxides obtained as described under Columbium, Tantalum, and Titanium less the sum of the weights of columbium pentoxide (obtained by zinc reduction), and titanium dioxide (obtained by color comparison), gives the weight of tantalum pentoxide, which, multiplied by 81.91 and divided by the weight of sample taken, gives the per cent tantalum. The weight of columbium pentoxide found by zinc reduction and titration is added to the weight of any columbium pentoxide found by color in the titanium dioxide precipitate to obtain the total columbium pentoxide, which weight multiplied by 0.6991 and by 2 gives the per cent columbium.

When reducing columbium solutions by means of a Jones reductor, the following precautions should be observed:

Prepare the reductor by adding 400 ml. of mercuric chloride solution (25 grams per liter) to from 800 to 850 grams of low iron 20-mesh zinc in an 800-ml. beaker; stir vigorously for 2 minutes, decant immediately, and wash with water and sulfuric acid (3 to 97). Zinc so prepared will serve for six determinations of high-columbium material. Reamalgamated zinc, while satisfactory for the reduction of iron or molybdenum, will lead to low results in the reduction of columbium. If the reductor has been idle, clean it by passing 100 ml. of cold sulfuric acid (3 to 97) and 50 ml. of water through it; then just prior to the reduction of each columbium solution, warm the reductor to about 70° C. by passing 200 ml. of almost boiling water through it. Discard the water, immediately connect the flask containing the ferric phosphate solution, and pass the solutions through the reductor in the order given above.

TITANIUM

To the filtrate from the columbium and tantalum (see Columbium, Tantalum, and Titanium) containing all the iron, chromium, and the bulk of the titanium, add 10 ml. of tartaric acid solution (500 grams per liter), and evaporate to a volume of approximately 150 ml. Add a slight excess of ammonium hydroxide, then 8 ml. of sulfuric acid (1 to 1), and pass in a brisk stream of hydrogen sulfide for 10 minutes. Filter through a 9-cm. paper containing a little ashless paper pulp into a 400-ml. beaker, wash from 12 to 15 times with sulfuric acid (1 to 99) saturated with hydrogen sulfide and containing 10 ml. of tartaric acid solution (500 grams per liter), and discard. Add a 1- to 2-ml. excess of ammonium hydroxide to the filtrate, and continue to pass hydrogen sulfide through the solution for about 5 minutes longer. Filter through a 9-cm. paper containing a little ashless paper pulp into a 600-ml. beaker, and wash the paper and iron sulfide precipitate from 12 to 15 times with ammonium sulfide water containing 10 grams of ammonium chloride and 10 grams of ammonium tartrate per liter. Reserve the precipitate for iron. Evaporate the filtrate to a volume of approximately 300 ml., add 30 ml. of concentrated hydrochloric acid, boil for several minutes, and cool to 15° to 20° C. Add a little ashless paper pulp and then an excess of a freshly prepared,

filtered, cold 6% water solution of cupferron, with vigorous stirring. An excess of the reagent is indicated when 1 drop forms a snow-white precipitate that rapidly disappears.

Add 1 to 2 ml. more of the cupferron solution, stir vigorously for several minutes, filter through two superimposed 11-cm. papers containing a little ashless paper pulp, and wash from 12 to 15 times with cold hydrochloric acid (1 to 9) containing 5 ml. of the cupferron reagent per liter. Ignite in a weighed 50-ml. platinum dish first at a low temperature to burn off the paper and finally at 1000° to 1050° C. for 15 minutes (to constant weight), cool, and weigh. Multiply by 0.5995 to obtain the weight of titanium. Combine with the titanium found in the columbium-tantalum precipitate by color comparison, and multiply by 200 to obtain the per cent titanium. The ignited and weighed titanium dioxide may be tested for columbium pentoxide as follows: Fuse with from 2 to 3 grams of potassium pyrosulfate, dissolve the cold melt by heating with 20 ml. of sulfuric acid, cool to room temperature, transfer to a 100-ml. volumetric flask, dilute to the mark with sulfuric acid, and mix thoroughly. Transfer a 25-ml. portion to a 50-ml. volumetric flask, add 20 ml. of phosphoric acid, mix thoroughly, and cool to room temperature. Dilute to the mark with sulfuric acid, and mix thoroughly. (Use only acids that have been previously slowly heated to 160° C. for 30 minutes and cooled in a desiccator to room temperature.)

Transfer a portion to a 1-cm. cell of a Beckman quartz spectrophotometer Model D (or similar apparatus), and read the null at a wave length of 350 millimicrons. Then add 1 drop of hydrogen peroxide (30%) to the solution in the 50-ml. volumetric flask, mix well, and read the density in another 1-cm. cell at the same wave length. The phosphoric acid used serves to prevent formation of the yellow color due to the titanium, but does not affect the columbium color which is also yellow. Prepare a graph set up on known amounts of pure columbium pentoxide under identical conditions. The weight of any columbium found is multiplied by 4 and by 1.43 to obtain the corresponding amount of columbium pentoxide in the titanium dioxide precipitate. Deduct the weight of columbium pentoxide found colorimetrically from the weight of the titanium dioxide precipitate and multiply the remainder by 0.5995 to obtain the weight of titanium. Add the weight of titanium found to that obtained in the columbium plus tantalum precipitate by color, and multiply by 200 to obtain the per cent titanium in the sample.

COBALT AND NICKEL

Electrolytic Method. Transfer 1.0000 gram of the 80- to 100-mesh sample to a 100-ml. platinum dish, add 20 ml. of hydrofluoric acid, cover, and then add 10 ml. of concentrated nitric acid a little at a time, with heating, until all action is over. Remove and rinse the cover with a little water and then rinse down the sides of the dish. Carefully add 20 ml. of concentrated sulfuric acid, stir well, and evaporate to dense fumes of sulfuric acid. Cool, transfer to an 800-ml. beaker, and rinse the dish successively with warm water, hot potassium hydroxide (200 grams per liter) to remove adhering tungstic acid, hot water, hydrochloric acid, and finally with hot water. Dilute to 300 ml., stir well, and digest for from 10 to 15 minutes at a temperature of approximately 75° C. to ensure the solution of all soluble salts. Dilute to 400 ml. with cold water, add a 20-ml. excess of potassium hydroxide solution (200 grams per liter) and 5 ml. of hydrogen peroxide (30%) diluted with an equal volume of water, and boil for several minutes.

Filter through an 11-cm. paper containing a little ashless paper pulp, and wash first from 12 to 15 times with hot potassium hydroxide solution (10 grams per liter), and then 10 or 12 times with hot water. Transfer the paper and precipitate to the beaker, add 25 ml. of concentrated nitric acid and 20 ml. of perchloric acid (70%), and evaporate to fumes of perchloric acid to ensure

the destruction of all organic matter. Cool, add 200 ml. of warm water, a 20-ml. excess of potassium hydroxide solution (200 grams per liter) and 5 ml. of hydrogen peroxide (30%) diluted with an equal volume of water, boil for several minutes, and filter and wash as before. Return the paper and precipitate to the beaker, add 25 ml. of concentrated nitric acid and 10 ml. of perchloric acid (70%), and evaporate to dense fumes of perchloric acid to destroy all organic matter. Cool, add 50 ml. of hydrochloric acid (1 to 6), heat to boiling for from 1 to 2 minutes to expel free chlorine, and cool to 15° to 20° C.

Add a little ashless paper pulp, and then a cold, freshly prepared, filtered 6% water solution of cupferron slowly, with vigorous stirring to precipitate the columbium, tantalum, titanium, and iron. An excess of the reagent is indicated when 1 drop forms a snow-white precipitate that rapidly disappears. Add 1 to 2 ml. additional of the cupferron reagent, stir vigorously for several minutes, filter (preferably by suction) through an 11-cm. paper containing a little ashless paper pulp into a 400-ml. beaker, and wash from 12 to 15 times with cold hydrochloric acid (1 to 9) containing 5 ml. of the cupferron reagent per liter. Add 25 ml. of concentrated nitric acid to the filtrate, evaporate to dense fumes of perchloric acid to destroy all organic matter, and continue the heating until the volume has been reduced to approximately 5 ml. Cool, add 10 ml. of sulfuric acid (1 to 1), and a few milliliters of sulfurous acid (6%), and evaporate to dense fumes of sulfuric acid to expel all perchloric acid. Cool, add 100 ml. of water, and heat to dissolve cobalt and nickel sulfates. Cool, add a slight excess of ammonium hydroxide, then sufficient sulfuric acid (1 to 1) to give a solution containing sulfuric acid (2 to 9) by volume, and pass in hydrogen sulfide for 15 minutes. Filter through a 9-cm. paper containing a little ashless paper pulp into a 400-ml. beaker, and wash the paper and any precipitate 18 to 20 times with hydrogen sulfide water containing sulfuric acid (1 to 199). The filtration may be omitted if no precipitate was formed during the hydrogen sulfide treatment indicating the absence of copper or any metals of the second group.

Boil the filtrate for at least 15 minutes to expel hydrogen sulfide, remove from the heat, carefully add 1 to 2 grams of ammonium persulfate, and continue the boiling for 5 to 10 minutes longer. Add 5 grams of c.p. urea or 5 ml. of sulfurous acid (6%) and further boil for several minutes. Cool, dilute to 200 ml. with cold water, add 10 grams of ammonium sulfate and a 20-ml. excess of fresh concentrated ammonium hydroxide, and electrolyze the sulfate solution with a current of 0.2 to 0.3 ampere, using a weighed platinum gauze cathode, and a spiral anode. If the electrolysis is allowed to run overnight, add an excess of 50 ml. of ammonium hydroxide. The gauze cathode cylinder should be completely submerged in the solution. When the deposition of the cobalt appears to be almost complete, add a mixture of 15 ml. of fresh ammonium hydroxide and 5 ml. of sulfurous acid (6%), continue the electrolysis until the solution becomes colorless, and then for at least 1 hour longer. Remove the cathode from the beaker, rinse thoroughly with water, and dip into 95% alcohol; dry for a few minutes at a temperature of 100° C., cool, and weigh. If not clear, filter the electrolyte through an 11-cm. paper containing a little ashless paper pulp, and wash the paper from 8 to 10 times with hot water.

To test the electrolyte for complete deposition of the cobalt and nickel, transfer the cold solution to a 500-ml. volumetric flask, dilute to the mark, and mix thoroughly. To test for cobalt transfer a 250-ml. portion to a 600-ml. beaker, acidify with hydrochloric acid, add 2 grams of citric acid and an excess of from 2 to 3 ml. of ammonium hydroxide, then add from 0.1 to 0.25 gram of phenylthiohydantoic acid, and boil for from 3 to 5 minutes. Remove from the heat, allow to stand for at least 15 minutes, filter through an 11-cm. paper containing a little ashless paper pulp, and wash from 12 to 15 times with ammonium chloride solution (20 grams per liter) containing 1 ml. of ammonium hy-

droxide. Ignite in porcelain first at a temperature of 500° to 600° C. to burn off the paper, and finally for 15 minutes (to constant weight) at 750° to 800° C.; cool and weigh as cobalt oxide, 73.4% of which is cobalt. Multiply the amount of cobalt found by 2 and add to that found by electrolysis to obtain the total cobalt.

To test for nickel, transfer the remaining 250-ml. portion to a 600-ml. beaker, acidify with hydrochloric acid, and add 2 grams of citric acid. Next add a slight excess of ammonium hydroxide and 5 ml. (or a sufficient amount) of a 3% acetone solution of dimethylglyoxime, heat to 70° to 80° C., and cool in cold water for 1 hour or longer. Filter through a weighed fritted-glass crucible, and wash first from 18 to 20 times with cold water and then with 25 ml. of acetone (12.5 ml. of acetone and 12.5 ml. of cold water). Heat in an electric oven first at 110° to 120° C. for 30 minutes and finally for 1 hour (to constant weight) at 150° to 160° C., cool, and weigh. Multiply the increase in weight of the crucible by 2, and then by 0.2032 to obtain the weight of nickel in the electrolysis filtrate. Add the nickel found to that obtained by electrolysis to obtain the total nickel in the sample.

To determine nickel and sulfur in the electrolytic deposit, dissolve the weighed deposit with 25 ml. of concentrated nitric acid in a 400-ml. beaker and rinse and remove the cathode. Cool the solution to room temperature, transfer to a 50-ml. volumetric flask, dilute to the mark, and mix thorougly. Withdraw 25 ml. of the solution and transfer to a 150-ml. beaker. (Reserve the remaining 25-ml. portion for the determination of nickel.) Add 0.5 gram of sodium nitrate and 10 ml. of perchloric acid (70%), and evaporate to dense fumes of perchloric acid to expel all nitric acid. Cool, add 50 ml. of water and 0.5 ml. of hydrochloric acid and boil for several minutes. Add 10 ml. of barium chloride solution (100 grams per liter), stir well, allow to stand overnight at room temperature, and filter through a 9-cm. tight paper containing a little ashless paper pulp. Wash from 18 to 20 times with hydrochloric acid (1 to 1000), ignite first in a 30-ml. platinum crucible at 500° to 600° C. and finally for 10 minutes at 750° to 800° C., cool and weigh. Deduct the blank on the reagents and multiply the remaining weight by 0.1374 and by 2 to obtain the weight of sulfur to be deducted from the deposited metal.

Transfer the 25-ml. portion reserved for nickel to a 400-ml. beaker and evaporate to a sirup (almost to dryness); then cool and dilute to 150 ml. with water. Place under a hood having a good draft, and add from 1 to 1.5 grams of potassium cyanide (a sufficient amount to dissolve the precipitate and render the solution slightly alkaline) a little at a time; this should ensure a clear solution that becomes alkaline, provided the nitric acid solution of the metal was evaporated as described. One gram of cobalt requires 7 grams of potassium cyanide to form the double soluble salt of potassium and cobalt; should the solution become slightly cloudy, add a little additional potassium cyanide. Too large an excess of potassium cyanide may result in incomplete precipitation of the nickel during the subsequent treatment with dimethylglyoxime. Add 2 ml. (or a sufficient amount to produce a honey yellow color) of hydrogen peroxide (30%) diluted with 5 ml. of water, and boil down to a volume of about 75 ml. to destroy the excess hydrogen peroxide.

Remove from the source of heat, dilute with warm water to 200 ml., and cool to 60° to 70° C. Add from 0.25 to 0.50 gram of dimethylglyoxime powder and from 5 to 10 ml. of formaldehyde, stir vigorously for several minutes, and allow to stand in cold water for 2 hours or preferably overnight if the nickel content of the sample is less than 0.25%. The formaldehyde (2) added does not break down the double cyanide of cobalt and potassium, but reacts with the nickel compound as shown in the following formula:

$$K_2Ni(CN)_4 + 2HCOH = Ni(CN)_2 + 2HCOH \cdot KCN$$
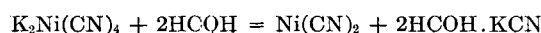
The nickel cyanide then reacts with the dimethylglyoxime, without interference from the cobalt. Filter through two superimposed 9- or 11-cm. papers (containing a little ashless paper pulp) supported in a Büchner funnel, moderate suction being employed, and wash from 20 to 25 times with cold water. Discard the filtrate. Wash the suction flask thoroughly with distilled water, connect with the Büchner funnel, and dissolve the nickel glyoxime precipitate off the filter with 50 ml. (or a sufficient amount) of hot hydrochloric acid (1 to 3). Wash the filter thoroughly with hot water and transfer the filtrate to the 600-ml. beaker. Add 5 ml. of tartaric acid solution (500 grams per liter), 10 ml. (or a sufficient amount to precipitate the nickel) of a 3% acetone solution of dimethylglyoxime, and a slight excess of ammonium hydroxide (1 to 1), dropwise, with vigorous stirring. Heat to 70° C., cool to room temperature in cold running water, and allow to stand for 1 hour or longer; filter through a weighed fritted-glass crucible and wash first from 18 to 20 times with cold water and then with 25 ml. of acetone (12.5 ml. of acetone and 12.5 ml. of water). Heat in an electric oven first at a temperature of 110° to 120° C. for 30 minutes, and finally at 150° to 160° C. for 1 hour (to constant weight), cool, and weigh. Multiply the increase in weight of the crucible by 0.2032 and by 2 to obtain the weight of nickel.

Potentiometric Method (1) for Cobalt. The determination may be completed by the potentiometric method as follows:

Return the paper and precipitate from the electrolytic method after making the double potassium hydroxide, etc., separation to remove the tungsten (and any small amount of molybdenum and chromium present) to the 600-ml. beaker, add 25 ml. of concentrated nitric acid and 10 ml. of perchloric acid (70%), and evaporate to dense fumes of perchloric acid to destroy all organic matter; continue the heating until the volume has been reduced to about 5 ml. and the larger part of the free perchloric acid has been expelled. Allow to cool, add 50 ml. of warm water and 2 ml. of concentrated nitric acid, boil for several minutes to expel free chlorine, and cool to 15° C. Measure an aliquot portion of the standard potassium ferricyanide solution (1 ml. = approximately 3.5 mg. of cobalt) from a buret into a 600-ml. beaker (using approximately 10 ml. in excess of that required to react with the cobalt in the sample), add 100 ml. of ammonium citrate solution and 80 ml. of concentrated ammonium hydroxide, dilute to 250 ml., and cool to about 15° C. Add the cold (about 15° C.) cobalt solution of the alloy slowly, with stirring, and rinse the beaker well with cold water, the final volume being approximately 400 ml., and immediately titrate the excess ferricyanide potentiometrically. Never add the ammoniacal potassium ferricyanide solution to the cobalt solution. The potentiometric end point is best if the solution is cooled to approximately 15° C. before adding the cobalt solution of the alloy. The cobalt is oxidized by the ferricyanide from a valence of 2 to 3 as shown in the equation:

$$Co^{++} + K_3Fe(CN)_6 \longrightarrow Co^{+++} + K_4Fe(CN)_6$$
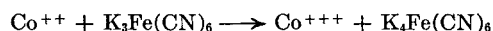
TITRATION. The end point in the titration of the excess ferricyanide with standard cobalt solution must be obtained potentiometrically. With the bright platinum calomel electrode system, the end point is sharp, although the change in potential is not great enough to permit the use of a single deflection type of end point such as is used in the titration of chromate with ferrous sulfate. To obtain the end point on a Beckman laboratory model pH meter, the switch is set at +MV, and the scale set to 2.5; then if an excess of ferricyanide is present the microammeter needle will be off the scale on the left side; however, if an insufficient amount (less than 5 ml.) of ferricyanide was taken, the needle may be off the scale on the right side, in which case the analysis should be repeated and an increased amount of ferricyanide used. The buret used to add the standard cobalt nitrate

solution should be calibrated for average drop size by counting the number of drops in 5 or 10 ml. of solution dropping from its tip. The standard cobalt nitrate solution is added cautiously until the needle returns to zero; then the solution is added dropwise, and the needle is brought back to zero after each addition; the change in scale reading with every drop is tabulated, and the maximum change in the scale reading is taken as the end point. After a few titrations have been made, the operator can easily locate this end point.

NOTE. Manganese is quantitatively titrated along with the cobalt and must be determined and the proper correction made.

Solutions Required. DIMETHYLGLYOXIME SOLUTION-3% ACETONE. Dissolve 3 grams of dimethylglyoxime in 95 ml. of C.P. acetone and 5 ml. of water, and filter. One milliliter will precipitate 7 mg. of nickel. Store in a cool place and do not use if more than 5 days old.

AMMONIUM CITRATE SOLUTION. Dissolve 800 grams of citric acid in 1600 ml. of cold, freshly distilled water, and add 1080 ml. of concentrated ammonium hydroxide.

STANDARD COBALT NITRATE SOLUTION (1 ml. = approximately 3 mg. of cobalt). Transfer 6.4 grams of cobalt metal (98% or better) to a 600-ml. beaker, cover, add 75 ml. of nitric acid (1 to 1), and warm gently until dissolved. Boil for several minutes to expel nitrous fumes, cool to room temperature, and add 100 ml. of cold water. Transfer to a 2-liter volumetric flask, dilute to the mark with cold, freshly distilled water, and mix thoroughly. Withdraw two 100-ml. aliquot portions by means of an accurately calibrated buret or pipet, and transfer to two 400-ml. beakers; cover, add 10 ml. of perchloric acid (70%) to each, and complete the determination of cobalt (+nickel) by electrolysis as described in the electrolytic method. Dissolve the deposit off one electrode in nitric acid and test for sulfur and nickel; deduct the weight of sulfur and nickel obtained from the combined cobalt (plus nickel) to obtain the amount of cobalt in the 100-ml. aliquot portion taken for the test, and from this calculate the percentage of cobalt in the solution.

STANDARD POTASSIUM FERRICYANIDE SOLUTION. Dissolve 40 grams of the salt in 100 ml. of cold, freshly distilled water, transfer to a 2-liter volumetric flask, dilute to the mark, and mix thoroughly. Standardize as follows: Transfer a 35-ml. accurately measured portion to a 600-ml. beaker, add 100 ml. of ammonium citrate solution and 80 ml. of concentrated ammonium hydroxide, dilute to 250 ml., and cool to 15° C. Next accurately measure 25 ml. of the standard cobalt nitrate solution into a 400-ml. beaker, dilute to 75 ml. with cold water, and cool to about 15° C.; then add slowly, with stirring, to the ammoniacal ferricyanide solution. Rinse the beaker well with cold water and dilute to 400 ml. with cold water (about 15° C.). Complete the titration of the excess ferricyanide with standard cobalt solution as described above. The ferricyanide solution should be kept in a dark-colored bottle and should be standardized at least every two weeks.

CALCULATIONS.

$$\frac{\text{Total ml. of Co solution used} \times \text{mg. of Co per ml.}}{\text{ml. of ferricyanide solution taken}} =$$

mg. of Co per ml. of ferricyanide

Let A = titer of standard ferricyanide solution in terms of cobalt obtained by titration of 35 ml. of the ferricyanide solution as described above.

Let B = titer of standard cobalt solution in terms of cobalt obtained electrolytically.

Let C = weight of Mn in the sample × 1.07 (to be deducted)

Then

$$\left[\frac{(\text{Ml. of } K_3Fe(CN)_6 \text{ taken} \times A) - (\text{ml. of } Co(NO_3)_2 \times B)}{\text{weight of sample taken}}\right] - C \times 100 = \% \text{ cobalt}$$

CHROMIUM

Treat 2 grams of the 80- to 100-mesh sample in a large platinum dish by the procedure described under Columbium, Tantalum, and Titanium; up to and including the double precipitation with ammonium hydroxide and filtration. Transfer the washed paper and precipitate to a 600-ml. beaker, add 25 ml. of concentrated nitric acid and 25 ml. of perchloric acid (70%), and evaporate to dense fumes of perchloric acid to destroy all organic matter. Allow to cool, add 300 ml. of hot water, 20 ml. of sulfuric acid

(1 to 1), and boil for several minutes to expel free chlorine. Add 15 ml. of silver nitrate solution (5 grams per liter), an excess of 5 or 6 drops of potassium permanganate solution (25 grams per liter), and from 2 to 3 grams of ammonium persulfate, and boil for at least 10 minutes. If the deep red color of permanganic acid fades from the solution on boiling, cool somewhat and add additional ammonium persulfate until the red color persists after at least 5 minutes' boiling. Add sufficient hydrochloric acid (1 to 3) to discharge the permanganic acid color, and continue to boil for from 5 to 10 minutes longer to ensure the complete removal of all chlorine; then cool to 15° to 20° C., and titrate potentiometrically with standard 0.02 N ferrous ammonium sulfate (1 ml. = 0.000347 gram of chromium).

IRON

Transfer the iron sulfide precipitate and paper (see Titanium) to the original 400-ml. beaker, add 10 ml. of concentrated nitric acid and 10 ml. of perchloric acid (70%), and evaporate to dense fumes of perchloric acid to destroy all organic matter and expel all nitric acid. Cool, add 50 ml. of water and 2 ml. of hydrochloric acid, and boil for several minutes. Reduce the iron with stannous chloride solution, adding an excess of 1 but not more than 2 drops. Cool to 15° to 20° C., add at one stroke 10 ml. of saturated mercuric chloride solution, stir well, and allow to stand for 3 minutes. Dilute to 300 ml. with cold, freshly boiled water, add 25 ml. of sulfuric acid (1 to 1) and 3 ml. of phosphoric acid (85%) or 15 ml. of "titrating mixture," and titrate with 0.02 N potassium dichromate (1 ml. = 0.001117 gram of iron) to a permanent purple end point, using a few drops of sodium diphenylaminesulfonate as indicator. Multiply the volume of 0.02 N potassium dichromate taken by 0.1117 and by 2 to obtain the percentage of iron.

Solutions Required. TITRATING MIXTURE. Dissolve 67 grams of manganese sulfate in water, dilute to 729 ml., add 138 ml. of phosphoric acid (85%) and 133 ml. of concentrated sulfuric acid (sp. gr. 1.84), and mix well.

SODIUM DIPHENYLAMINESULFONATE INDICATOR. Dissolve 0.32 gram of the barium salt in 100 ml. of hot sodium sulfate (100 grams per liter), allow the barium sulfate to settle, and decant the clear supernatant liquid. Store in a dark-colored bottle.

SILICON

Transfer 1 gram of the 80- to 100-mesh sample and 10 grams of dry sodium peroxide to a 30-ml. iron crucible and mix thoroughly with a platinum or iron rod. Grasp the crucible with a pair of metal tongs and fuse carefully by revolving it in the outer edge of the flame of a laboratory burner at a temperature of 700° to 800° C. until the entire mass has blackened; as the mixture begins to fuse, rotate the crucible vigorously to keep the heavy particles of the sample in suspension and increase the temperature to approximately 900° C. for 3 to 5 minutes. Goggles should be worn when making this fusion.

Allow the crucible to cool almost to room temperature, cover with a nickel lid, and tap on a solid object to loosen the melt. Transfer the cake to a dry 500-ml. porcelain casserole of good glaze, cover, and add 75 ml. of concentrated hydrochloric acid. Rinse the crucible with at least 25 ml. of warm water and add the rinsings to the casserole. Next add 100 ml. of perchloric acid (70%) and evaporate slowly to fumes of perchloric acid; continue the fuming of the acid for at least 10 minutes longer, and take care to avoid too great a loss of perchloric acid by volatilization.

Allow the mass to cool somewhat, add 250 ml. of warm water, and stir well. Filter through an 11-cm. paper containing some ashless paper pulp into a 600-ml. beaker, and wash the paper and precipitate at least 25 times with hydrochloric acid (1 to 99); reserve the paper, silica, and tungstic acid precipitate.

Add a very slight excess of ammonium hydroxide (1 to 1) to the nearly boiling filtrate, boil for 1 minute, filter through a 12.5-cm. paper containing some ashless paper pulp, and wash 18 to 20 times with hot ammonium chloride solution (20 grams per liter) containing 1 to 2 drops of ammonium hydroxide. Transfer the washed precipitate to the 500-ml. porcelain casserole, add 40 ml. of concentrated nitric acid and 50 ml. of perchloric acid (70%), evaporate slowly to fumes of perchloric acid, and continue the fuming of the acid for at least 10 minutes longer. Allow to cool somewhat, add 250 ml. of warm water, stir well, filter through an 11-cm. paper containing some ashless paper pulp, and wash 18 to 20 times with hydrochloric acid (1 to 99). Combine the paper and silica with the paper, silica, and tungstic acid precipitate reserved in the preceding paragraph, transfer to a 50-ml. platinum dish, and ignite at a temperature of 600° to 700° C. to burn off the paper. Cool and brush into a 300-ml. platinum dish. Add 25 grams (weighed on a rough balance) of powdered sodium pyrosulfate, mix thoroughly, and fuse carefully over a free flame at a temperature of about 750° C. to obtain a clear fusion. Cool somewhat, add 75 ml. of concentrated sulfuric acid and 1 to 2 ml. of perchloric acid (70%), and heat until the fusion has dissolved and copious fumes of sulfuric acid are freely evolved.

Cool somewhat, pour into an 800-ml. beaker containing 500 ml. of cold tartaric acid solution (80 grams per liter), and rinse the dish well with lukewarm tartaric acid solution (50 grams per liter) using a policeman, if necessary, to remove any silica adhering to the dish. Stir well and heat for a few minutes at a temperature not exceeding 60° to 70° C., for temperatures near boiling will result in the precipitation of some of the tungsten. Filter through an 11-cm. paper containing a little ashless paper pulp and wash at least 25 times with tartaric acid solution (50 grams per liter). The fusion with sodium pyrosulfate, fuming with sulfuric acid, and taking up the sodium pyrosulfate–sulfuric acid solution in tartaric acid, filtering, and washing as described serve to separate the tungstic, columbic, and tantalic acids from the silica.

Ignite in a 30-ml. platinum crucible first at about 600° C. to burn off the paper and, in case considerable tungsten, etc., remain, transfer the ignited precipitate to a 100-ml. platinum dish, add 5 grams of sodium pyrosulfate, mix, and fuse at 750° C. Cool, add 20 ml. of concentrated sulfuric acid, and heat to obtain a clear solution and to dehydrate the silica. Cool, pour into 300 ml. of cold tartaric acid solution (80 grams per liter) and proceed as described above. If, on the other hand, the silica precipitate appears to be almost, if not entirely, free from tungsten, etc., ignite it for 10 minutes at 1100° to 1150° C., cool in a desiccator, and weigh. Add several drops of sulfuric acid, 1 to 2 ml. of hydrofluoric acid, and evaporate to dryness. Ignite at 750° to 800° C. for 15 minutes, cool, and weigh. The loss in weight represents silica. Run a "blank" determination including the fusion of the sodium peroxide in the iron crucible and take the cold melt up in concentrated hydrochloric acid as described in the procedure. Dilute to 300 ml. with boiling water, add 5 grams of ammonium chloride and a very slight excess of ammonia, boil for 1 minute, filter, and complete the determination as described. Deduct the weight of the blank found from the weight of silica found on the 1-gram sample of alloy, and multiply the net weight by 46.72 to obtain the percentage of silicon in the sample.

MANGANESE

Treat 1 gram of the 80- to 100-mesh sample exactly as described for cobalt and nickel up to and including the treatment of the second potassium hydroxide precipitate with 25 ml. of con-

centrated nitric acid and 10 ml. of perchloric acid (70%), and evaporation to dense fumes of perchloric acid. Allow to cool somewhat, add 100 ml. of water, and boil for several minutes to expel free chlorine. Then add 10 ml. of sulfurous acid (6%), boil for 5 minutes, and allow to digest at approximately 75° C. for 15 to 30 minutes, or until the supernatant liquid is clear. Filter through a 9-cm. paper containing a little ashless paper pulp into a 400-ml. beaker, and wash the paper and precipitate 12 to 15 times with sulfuric acid (1 to 99); discard the precipitate. Add to the filtrate 10 ml. of sulfuric acid (1 to 1), 10 ml. of phosphoric acid (85%), and approximately 0.5 gram of potassium periodate, boil for 3 minutes, and cool to room temperature.

Table I. Analysis of Tungsten Carbide

Sample No.	% W	% Cb	% Ta	% Ti	% Co	% Ni	% Mo	% Fe	% Cr	% Mn	% Si	% C
1	64.28	1.75	9.50	6.47	10.03	0.19	0.01	1.05	0.05	Trace	a	6.66
2	64.10	2.20	9.78	6.44	9.04	0.09	0.02	0.96	0.04	Trace	a	7.04
3	60.26	Nil	Nil	18.75	7.25	0.15	0.08	4.70	0.60	0.05	0.06	7.86
4	86.35	0.36 b	..	..	5.74 c	..	a	1.50	0.04	Trace	a	5.64
5	84.00	Nil	Nil	Nil	8.16 c	..	a	1.96	0.08	Trace	a	5.51
6	86.94	Nil	Nil	Nil	6.08 c	..	a	0.98	0.23	...	a	5.66
7	77.35	Nil	1.30	4.14	9.29 c	..	a	1.20	..	...	a	6.24

a Not determined.
b Columbium + tantalum.
c Cobalt + nickel.

Dilute to exactly 250 ml. and measure the transmittancy in a 1-cm. cell of a Beckman quartz spectrophotometer Model D at a wave length of 575 millimicrons and a slit width of 0.04 mm. after first having set the 100% transmittancy on distilled water. To prepare a standard calibration curve, add 0.1 to 1 mg. (or that required to cover the manganese range) of manganese in the form of 0.01 N potassium permanganate to 100 ml. of water containing 10 ml. of sulfuric acid (1 to 1), 10 ml. of phosphoric acid (85%), and approximately 0.5 gram of potassium periodate, boil for 3 minutes, cool, dilute to 250 ml., and measure the transmittancy in a Beckman quartz spectrophotometer as described. A correction of 0.01% manganese should be made for each 10% cobalt present.

CARBON

Transfer 1 factor-weight (0.2727 gram) of the 80- to 100-mesh sample to a zirkite or Alundum boat (4.5 inches long by 1 inch wide by 0.6 inch deep, approximate inside diameter) provided with a bed of 90-mesh Alundum molded in the form of a trench, cover the alloy with 2 grams of iron drillings, and sprinkle a layer of well ignited cupric oxide over the top of the charge. Insert the boat and its contents into a combustion tube heated at 1100° to 1150° C., and after 1 minute turn on the oxygen at the rate of 800 to 1000 ml. per minute. When combustion appears to be complete, reduce the rate of oxygen flow to approximately 600 ml. per minute; sweep the tube for 8 to 10 minutes and absorb the evolved carbon dioxide in Ascarite, and weigh. Run a blank on all of the materials used, except the sample, and deduct. Multiply the net weight of carbon dioxide found by 100 to obtain the percentage of carbon.

Table I gives the analyses of some samples of tungsten carbide containing columbium, tantalum, and titanium; tantalum and titanium; titanium; and others that contain neither columbium, tantalum, nor titanium.

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Determination of Deuterium in Water

A Mass Spectrometric Method

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A procedure is given for the determination of deuterium in water of any isotopic composition. The procedure is simple and rapid when the equipment is available. The method does not, in general, require any removal of dissolved impurities as would be the case for a specific gravity method. The water sample may be recovered practically unchanged after the analysis is completed.

SINCE its discovery in 1932 by Urey, Brickwedde, and Murphy (*12*), deuterium, the mass two isotope of hydrogen, has found much use in scientific work in the form of heavy water. Biological tracer studies using deuterium have revealed useful information. Several organic reaction mechanisms have been worked out using heavy hydrogen (*5*). More recently heavy water has come into prominence in the field of atomic energy as a moderator—i.e., as a slowing down agent for neutrons (*10*).

Any physical or chemical property of light and heavy hydrogen or water may be used as the basis of a method for the analytical determination of deuterium, provided that the difference in that property between the two isotopes and the experimental ability of measurement are sufficient to provide the desired degree of precision and accuracy. Specific gravity methods involving both float and pycnometer have been used with good results. Refractive indices (*2*), atomic spectra (*12*), thermoconductivity of hydrogen gas (*3*), thermoconductivity of water vapor (*1*), infrared absorption (*6*), freezing point (*7*), viscosity (*8*), and potentials of light and heavy hydrogen electrodes (*11*) have all been used with varying degrees of success as the bases of methods for the determination of deuterium in water.

Mass spectrometer methods cannot be performed directly upon water molecules because water vapor is readily adsorbed to an appreciable extent on the inner surfaces of the apparatus. Preparation of hydrogen gas from water makes mass spectrometer analysis satisfactory. Decomposition of water by electrolysis and by chemical reduction have proved unsatisfactory, however. A successful method of preparation of a hydrogen gas corresponding to a given water sample involves the equilibration reaction between the hydrogen isotopes in the water specimen and in a hydrogen gas. The first equilibration was performed by Farkas (*4*) in 1936. The general method was developed and used for the analysis of water specimens very near to normal deuterium abundance and very near to pure deuterium oxide early in the Manhattan Project. This paper extends the method to one of general applicability for the determination of deuterium in water specimens of any deuterium-protium ratio.

THEORETICAL

This method of determining deuterium in water involves an equilibration of the water sample with hydrogen gas and subsequent analysis on the mass spectrometer of the equilibrated gas. Inasmuch as the result of a water analysis must be calculated from an observed gas composition, it is necessary to establish some mathematical basis upon which the water isotopic composition may be calculated from the experimental data.

The equilibration reaction must proceed through two general

steps: evaporation of the water, each type of liquid water molecule (H_2O, HDO, and D_2O) being in dynamic equilibrium with the corresponding water vapor molecule, as well as in equilibrium with each other; and dynamic equilibrium reactions between the water vapor molecules and the hydrogen gas molecules (H_2, HD, and D_2). A catalyst is required for the latter step, and platinum oxide, Adams' catalyst, has been found satisfactory.

The derivation must be based upon all the equilibria involved and is carried out as follows:

The following equilibria must be satisfied:

$$H_2O(g) + D_2O(g) = 2HDO(g) \quad K_1 = \frac{[HDO(g)]^2}{[H_2O(g)][D_2O(g)]} \quad (1)$$

$$H_2O(g) + HD = HDO(g) + H_2 \quad K_2 = \frac{[HDO(g)][H_2]}{[H_2O(g)][HD]} \quad (2)$$

$$HDO(g) + D_2 = D_2O(g) + HD \quad K_3 = \frac{[D_2O(g)][HD]}{[HDO(g)][D_2]} \quad (3)$$

$$H_2 + D_2 = 2\,HD \qquad K_4 = \frac{[HD]^2}{[H_2][D_2]} \quad (4)$$

$$H_2O(l) = H_2O(g) \qquad K_5 = \frac{[H_2O(g)]}{[H_2O(l)]} \quad (5)$$

$$HDO(l) = HDO(g) \qquad K_6 = \frac{[HDO(g)]}{[HDO(l)]} \quad (6)$$

$$D_2O(l) = D_2O(g) \qquad K_7 = \frac{[D_2O(g)]}{[D_2O(l)]} \quad (7)$$
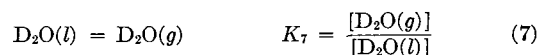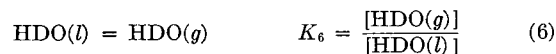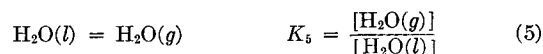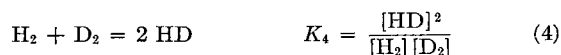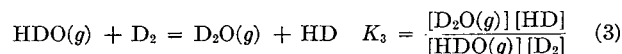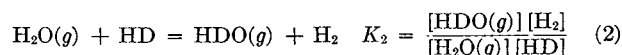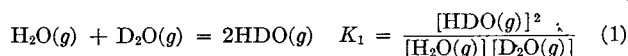
Any other possible combination between gas and/or water molecules is mathematically equivalent to some combination of these equilibria.

Multiply K_2 by K_5, divide by K_6, and transpose:

$$[H_2O(l)] = \frac{K_6}{K_2K_5} \times \frac{[H_2][HDO(l)]}{[HD]} \quad (8)$$

Multiply K_3 by K_6, divide by K_7, and transpose:

$$[D_2O(l)] = \frac{K_3K_6}{K_7} \times \frac{[D_2][HDO(l)]}{[HD]} \quad (9)$$

A system of units for the liquid concentrations must be established. Any consistent units are permissible; the units will be defined as mole per cent of the total—that is,

$$[H_2O(l)] + [D_2O(l)] + [HDO(l)] = 100 \quad (10)$$

Substitute Equations 8 and 9 into 10; and solve for [HDO(*l*)]:

$$[HDO(l)] = \frac{K_7K_2K_5[HD]100}{K_7K_2K_5[HD] + K_2K_5K_3K_9[D_2] + K_6K_7[H_2]} \quad (11)$$

From Equations 8 and 9 with 11, solve for [$H_2O(l)$] and [$D_2O(l)$] in terms of gas concentration:

$$[H_2O(l)] = \frac{K_6K_7\,100\,[H_2]}{K_7K_2K_5[HD] + K_3K_6K_2K_5[D_2] + K_6K_7[H_2]} \quad (12)$$

$$[D_2O(l)] = \frac{K_3K_6K_2K_5\,100\,[D_2]}{K_7K_2K_5[HD] + K_3K_6K_2K_5[D_2] + K_6K_7[H_2]} \quad (13)$$

Because the concentrations are already defined in mole per cent units, the mole % D in the water may be expressed as:

$$\text{Mole \% D in water} = [D_2O(l)] + \tfrac{1}{2}[HDO(l)] \qquad (14)$$

Substitute Equations 11 and 13 into 14:

Mole % D in water =

$$\frac{K_3K_6K_2K_5\,100\,[D_2] + K_7K_2K_5\,50\,[HD]}{K_7K_2K_5[HD] + K_3K_6K_2K_5[D_2] + K_6K_7[H_2]} \qquad (15)$$

Equation 15 is the equation for water isotopic composition in terms of the equilibrated gas composition and the equilibria constants involved in the reaction.

Insert the values for the constants into Equation 15 (all these values are correct at 25° C.):

$K_2 = 3.62$

$K_3 = 3.11$

$K_5 = P_{H_2O}$

$K_6 = P_{HDO}$

$K_7 = P_{D_2O}$

and using the relationship $\dfrac{P_{D_2O}}{P_{HDO}} = \left(\dfrac{P_{D_2O}}{P_{H_2O}}\right)^{1/2} = 1.067$

$$\text{Mole \% D in water} = \frac{1055[D_2] + 159.0\,[HD]}{3.179[HD] + 10.55[D_2] + 0.8231\,[H_2]} \qquad (16)$$

Equation 16 may be used to calculate the isotopic composition of the water from the experimentally determined composition of the equilibrated gas. The equation holds good for the reaction at 25° C. for any composition of water. The gas molecule concentrations may, of course, be expressed in any consistent set of units; mole per cent of each gas species is probably the most convenient set of units to use. This equation could be simplified to eliminate one of the three types of gas molecules, from the calculation, yet it has been found advisable to keep it as given above.

EXPERIMENTAL.

A series of water standards of known isotopic composition was prepared by weight dilution methods, using normal distilled water and nearly pure deuterium oxide as the ingredients. For each analysis about 5 ml. of the water specimen, a few milligrams of platinum oxide catalyst, and an atmosphere of equilibrating gas were introduced into a small flask, about 30 ml. in volume. The flask and its contents were allowed to stand for about 1 hour, during which time the equilibration reaction proceeded to equi-

Table I. Water Analyses

Calcd. Mole % D	Exptl. Mole % D
49.4	48.4
24.9	26.1
78.9	77.3
57.5	55.6
37.7	36.0

librium. Analyses were performed on two separate portions of each water standard, using tank hydrogen and tank deuterium, respectively, as the equilibrating gases. In this manner it was possible to approach the state of equilibrium from both directions for each water specimen. After the reaction had proceeded to equilibrium, the gas was analyzed on a mass spectrometer of the Nier type (9). In several cases the gas was reanalyzed after standing for a considerably longer period of time with the water specimen and catalyst to provide a check on whether or not the reaction had been at equilibrium the first time. Corrections were applied to all gas analyses to eliminate error from dilution or concentration of the water by the gas during the reaction.

The results of the analyses are given in Table I.

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Determination of Major Constituents of Cedar Oil Vapor in Cedar Chests

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A procedure is given for rapid colorimetric determination of cedrene and cedrol in the air of cedar chests. The method is based on a red-violet color formation resulting from the reaction of cedrene with vanillin in the presence of hydrochloric acid. The cedrol is dehydrated in situ by phosphoric acid and determined as cedrene.

CEDAR chests are made from the heartwood of the eastern red cedar (Juniperus virginiana). The aroma in these chests is due to the volatile oil which is present in cedar wood to the extent of about 2%. Rabak (3) found the principal constituents of this oil to be sesquiterpenes, a hydrocarbon, cedrene ($C_{15}H_{24}$), and an alcohol, cedrol ($C_{15}H_{26}O$). In this investigation a method has been developed for the determination of these volatile constitutents in cedar chests.

Semmler (6), Ruzicka (5), and Treibs (7) determined in principle the structural formulas of these compounds. Cedrol was found to have a tertiary alcohol group and could be dehydrated with formic acid to produce cedrene, which had a double bond. Rosenthaler (4) discovered that turpentine reacted with vanillin in hydrochloric acid to give a green coloration. Bogatskii (1) applied this reaction to a quantitative colorimetric method for turpentine and found that compounds containing active

double bonds such as pinene and dipentene also reacted with this reagent.

EXPERIMENTAL

Preliminary experiments showed that cedrene in ethanol reacted with vanillin in hydrochloric acid to produce a red-violet color, whereas cedrol did not react under these conditions. It was found that 1% vanillin in hydrochloric acid formed a pink color which masked the violet coloration caused by cedrene, but that 0.1% vanillin was satisfactory. To produce a stable color it was necessary to use a volume of vanillin–hydrochloric acid reagent equal to that of alcoholic cedrene. Cedrol in ethanol was easily dehydrated by phosphoric acid to cedrene, which was then determined colorimetrically. Thus by using two aliquots of an ethanol solution of the unknown, it was possible to determine the total of cedrene plus cedrol as well as cedrene alone. The cedrol content was then found by difference.

REAGENTS

Ethanol, 95%. Ortho phosphoric acid, 85%.
Vanillin hydrochloric acid reagent, 0.1 gram of vanillin placed in a 100-ml. volumetric flask and made up to volume with concentrated hydrochloric acid. This reagent was most satisfactory when freshly prepared.
Standard solutions of cedrene in 95% ethanol were prepared, containing 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 mg. of cedrene per ml.
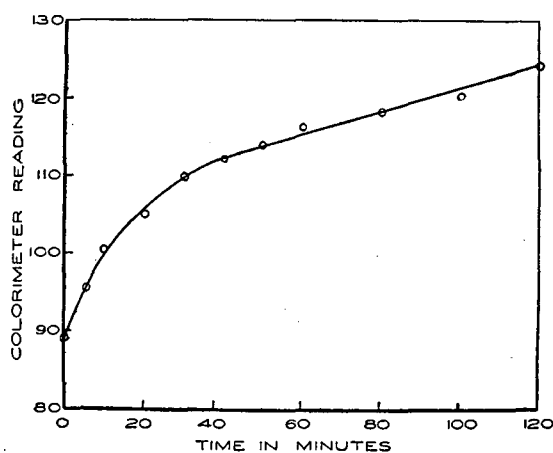
Figure 1. Color Stability
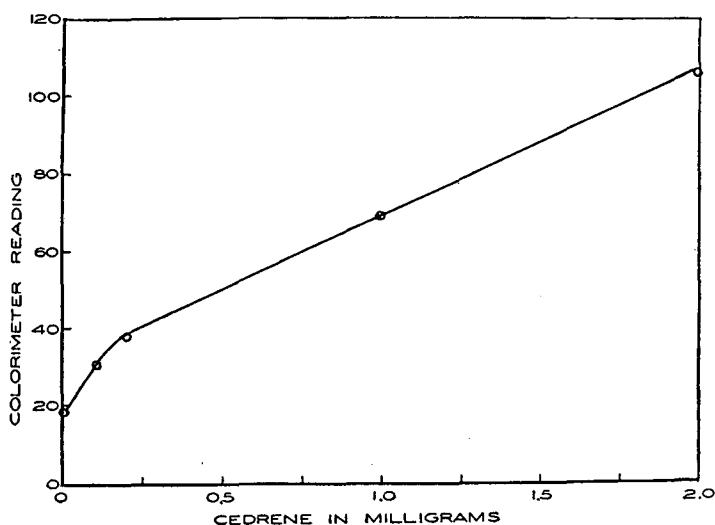
Figure 2. Determination of Cedrene
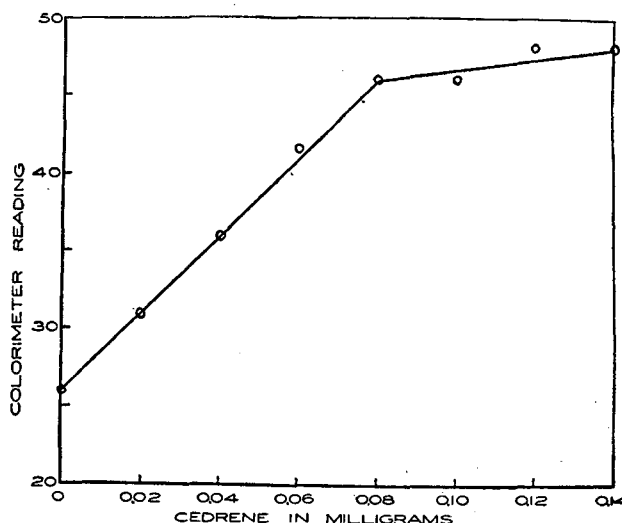
Figure 3. Cedrene at Low Concentrations
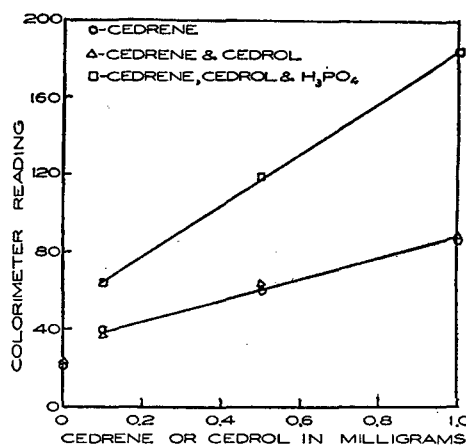
Figure 4. Cedrene-Cedrol Mixtures

APPARATUS

A Klett-Summerson photoelectric colorimeter equipped with green filter. Colorimeter tubes, graduated at 5 and 10 ml. Pipets of assorted sizes, 1 to 5 ml.

Gas sampling tube, large size, 2 to 4 liters. Gas absorption tube, microadaptation of Nichols (2) air lift pump gas absorber built in 18 × 150 mm. side-arm test tube.

PROCEDURE

Sampling. The lock is removed from the chest being tested and a rubber stopper containing a glass tube is inserted in the lock hole. Inside the chest is attached a rubber tube of such length that the air sample is obtained from the middle of the chest. The outlet of the absorber is connected to the top of a large water-filled gas sampling tube used to draw the air sample through the absorber. The volume of water removed from this tube is equal to the volume of air in the sample.

In practice the chest under test is closed and the outer rubber tube is clamped. After sufficient time for the chest to reach equilibrium has elapsed, 10 ml. of ethanol are placed in the absorption tube and 1 liter of air is drawn through slowly. Aliquots of this solution are used for analysis.

Analysis. Aliquots of standard and unknown solutions in alcohol are pipetted into colorimetric tubes and 1 ml. of phosphoric acid is added to the samples in which it is desired to determine the total of cedrene plus cedrol. These samples are shaken to ensure mixing and allowed to stand for 30 minutes to complete the dehydration of cedrol.

All samples are then diluted to the 5-ml. mark with ethanol and 5 ml. of the vanillin–hydrochloric acid reagent are added. Uniformity of the solutions is assured by inverting the tubes five times and allowing them to stand at least 30 minutes before color intensities are read.

Color intensities are determined with a Klett-Summerson photoelectric colorimeter equipped with a green filter. A tube of ethanol is used for the zero setting of the instrument and a blank is run along with the samples using alcohol alone.

RESULTS

To ascertain the stability of the color formed, the color intensity of a sample was determined at frequent intervals over a period of 2 hours (Figure 1). The rapid initial increase in intensity is due to the course of the reaction of cedrene with vanillin. The slower linear increase with time after the first 30 minutes is believed to be due to the concentration of color caused by contraction of the solution on cooling. Later work showed that no appreciable fading occurred after 16 hours.

That the change of color intensity with cedrene concentration was essentially linear in the range of 0.1 to 2.0 mg. of cedrene per determination is demonstrated by the data plotted in Figure 2. A similar linearity but a different slope was observed over the range of 0 to 0.1 mg. of cedrene (Figure 3). As little as 0.01 mg. of cedrene or cedrol was detectable. Experiments showed that the determination of cedrene was unaffected by the presence of cedrol, as shown by coincidence of the two curves in Figure 4.

The total of cedrene plus cedrol was determined by the use of phosphoric acid. This is clearly shown by the increased slope of the curve in Figure 4 when phosphoric was used.

When the method was applied to the analysis of air from cedar chests, values of 0.05 to 0.6 mg. of cedrene or cedrol per liter of air were obtained. It is probable that such unsaturated minor constituents as cedrenene and cedrenol also react with vanillin-hydrochloric acid reagent and are thus calculated as cedrene.

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Determination of Alumina in Iron Ore

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A new procedure for the separation of alumina in iron ore, which is not dependent upon a carefully controlled pH for its efficiency, involves the formation of ferrous-bipyridine complex not precipitated by ammonium hydroxide or carbonate. By the process as described, aluminum in small amounts can be separated from large amounts of iron in one precipitation. A procedure is described for the recovery in high yield of the masking reagent bipyridine. The cost of reagent required per determination is at a minimum.

THE determination of alumina in an iron ore is rendered difficult by two factors: the chemical similarity of ferric oxide and alumina, and the fact that alumina almost always comprises less than 2% of the mixture (often much less).

The problem has been approached from many directions and attacked with great persistence and diligence (5). A recent survey of some of the schemes has resulted in the choice of the phenylhydrazine method of Hess and Campbell (8) as modified by Allen (1) and by Golowaty and Ssidorow (6). A purely physical method for the separation, which is capable of giving highly accurate results, is the removal of iron with a mercury cathode (2). The method was originally described for the determination of vanadium in steel but is as efficacious for aluminum (3).

The chemical methods that are used for the separation of alumina from iron ore require several steps and repeated precipitations for accurate work. The hydrochloric acid–ether method of Gooch and Havens (7) is useful if the iron is not in too great concentration, but would not be used for iron ores.

Ferrari (4) observed that the ferrous complex of 2,2′-bipyridine gave no precipitate with ammonium hydroxide and that alumina could be precipitated in the presence of 2,2′-bipyridine. His work was conducted on synthetic samples and was of only cursory nature. The samples employed by Ferrari did not contain the great preponderance of iron found in an iron ore.

The experiment was first tried on synthetic samples made up with known aluminum-iron ratios (Table I). Ammonium alum

(Mallinckrodt's U.S.P.) was chosen as the source of aluminum because of its low aluminum content. Because this is a hydrated salt, it was analyzed before use and stored in a tight container after analysis. The source of iron was a sample of Mallinckrodt's reagent ferric alum. A blank on 6 grams gave an alumina precipitate of less than 0.1 mg. The analysis was conducted by ignition to the oxide and precipitation of hydrated alumina and ignition.

The 2,2′-bipyridine used was a commercial sample obtained from the G. Frederick Smith Chemical Company. To test for freedom from objectionable material, a 3-gram sample was

Table I. Analyses of Synthetic Samples

Method of Analysis	Al_2O_3 Found, %
Ignition	{11.40 Calculated for $NH_4Al(SO_4)_2.12H_2O$ {11.36
Precipitation	{11.25 Al_2O_3 = 11.24% {11.25

Table II. Separation of Aluminum from Iron in Sulfuric Acid Solution (Hydrochloric Acid Absent)

Sample No.	Al_2O_3 Taken $Mg.$	$Al_2O_3/Mg.Fe_2O_3$ $Mg.$	Al_2O_3 Found $Mg.$
1	131.4	1/1.27	131.9
2	25.5	1/7.42	25.4
3	25.5	1/39.2	29.6
4	12.1	1/82.6	15.7
5	14.3	1/70.0	14.3

Table III. Separation of Aluminum from Iron in Hydrochloric Acid Solution

Sample No.	Al$_2$O$_3$ Taken Mg.	Al$_2$O$_3$/MgFe$_2$O$_3$ Mg.	Al$_2$O$_3$ Found Mg.
1	17.3	1/57.8	17.2
2	11.2	1/89.4	11.8
3	11.9	1/84.0	11.6
4	11.7	1/85.5	11.7
5	13.2	1/75.8	13.4

ignited in a Vycor crucible; ash obtained weighed less than 0.1 mg.

The first problem was the complete reduction of iron, inasmuch as the complex with 2,2'-bipyridine forms only with the ferrous ion. Various methods of reduction were tried. Very complete reduction must be achieved, as about one hundred-fold excess of iron is present, and any unreduced iron will contaminate the alumina. Hydrazine and hydroxylamine were tried without complete success. Sodium bisulfite reduced the iron in weakly acidic solution quantitatively to the ferrous state. This reduction was very slow, even at higher temperatures, in an acidified sulfate solution; but the addition of a small amount of hydrochloric acid or a soluble chloride to the sulfate solution renders the reduction almost instantaneous in the warm solution. In the authors' experience this phenomenon was much more pronounced than the statement of Hillebrand and Lundell (9) might lead the uninitiated to expect. This is not easily explained. The formal potentials in dilute sulfuric and hydrochloric acids are not markedly different (10). This matter would seem to be rather abstruse and worthy of careful investigation.

DETERMINATION OF ALUMINA

Synthetic iron ore samples were prepared by dissolving weighed amounts of ammonium aluminum sulfate and ammonium ferric sulfate in about 300 ml. of water to which 1 ml. of concentrated sulfuric acid was added. A 25% excess of sodium bisulfite was added and the solution warmed to speed the reduction of the iron. The reduction in this case is slow and often not complete. When the reduction was finished and the solution had cooled, a 10% excess of 2,2'-bipyridine in 15 to 20 ml. of ethanol was added with stirring. A red solution was formed and it was not possible to use an indicator to determine the addition of enough ammonium hydroxide. A saturated solution of ammonium carbonate was used in the precipitation, as a slight excess did not have a solvent effect on the alumina. If thiocyanate is used to test complete reduction of the iron, an insoluble precipitate of [Fe(C$_{10}$H$_8$N$_2$)$_3$] (SCN)$_2$ is formed on the addition of 2,2'-bipyridine and must be removed before the precipitation of alumina.

The precipitated alumina, with added filter pulp, was filtered (the use of slight suction is recommended) through a Carl Schleicher and Schuell 589 blue ribbon filter paper and washed with a 2% ammonium nitrate solution which was brought to the transition point of methyl red with ammonium carbonate. The precipitate was washed until the red color of the ferrous-bipyridine complex ion was removed. The alumina was strongly ignited and weighed in a platinum crucible.

Table II shows that the results tend to be high, owing to the difficulty of complete reduction of the ferric ion Any unreduced iron will not form the complex and so is precipitated with the alumina. In each case a strong odor of sulfur dioxide could be noted over the warm solution after heating was stopped (after about 30-minute digestion). The procedure described, which gave results as shown in Table II, is not recommended.

This procedure was repeated with the substitution of a ferric chloride solution that contained the equivalent of 0.100 gram of ferric oxide and 0.04 ml. of concentrated hydrochloric acid per milliliter (Table III). Concentrated hydrochloric acid was added in place of concentrated sulfuric acid. The reduction of the ferric ion with bisulfite was both rapid and smooth.

The samples of iron ore selected for evaluating the accuracy of the present procedure were three in number: National Bureau of Standards Crescent iron ore, No. 26; another Bureau of Standards sample magnetite ore, No. 29a (the latter sample is pro-

vided only with a provisional certificate which states the alumina content); and a zenith hematite iron ore which has been carefully analyzed independently by many careful analysts and whose alumina content has been established authoritatively.

As a check of the scheme of analysis it is sufficient to report apparent alumina. This is usually considered alumina, titania, and phosphoric anhydride.

The analyses were conducted on samples of about 1 gram of the iron ore. The sample was accurately weighed and the silica dehydrated twice with 15 ml. of concentrated hydrochloric acid. It is necessary to remove the silica with hydrofluoric acid, fuse the residue with sodium bisulfate, and return the dissolved residue to the sample for analysis. The amount of alumina carried into the silica varies with the ore. In their samples the authors found that more alumina is carried into the silica in the case of the hematite ore than in the magnetite ores.

The filtrate from the dehydration of silica and the return of the residue, as described above, is treated in the same fashion as the synthetic samples. One might expect trouble with ores high in calcium oxide from the precipitation of calcium carbonate if ammonium carbonate is used as the precipitant. This can be avoided by the addition of ammonium chloride (about 5 grams for each sample) before precipitation, or by dissolving the precipitated alumina in warm dilute hydrochloric acid and reprecipitating with ammonium hydroxide, using methyl red as an indicator.

Dilute solutions of ammonium carbonate, and more especially the wash solution of ammonium nitrate and ammonium carbonate, provide media for growth of microorganisms. These are objectionable in that the by-products of their metabolism seem to increase markedly the solubility of alumina. These solutions should either be freshly prepared or so protected that they will not be infested. The addition of a few drops of toluene decreases the rate of growth of the microorganisms. It is, however, better to prepare the wash solutions freshly for use and thus eliminate this source of possible error.

Analyses of the various iron ores are included in Table IV. In each case the ignited alumina precipitate was snow-white.

Table IV. Analysis of Iron Ores

Sample	Weight, Grams		Al$_2$O$_3$ Found, %	Al$_2$O$_3$ Contained, %
	Sample	Al$_2$O$_3$		
1 Zenite	1.0220	0.0145	1.42	1.41
2 {N.B.S. Crescent	1.0849	0.0135	1.24}	1.18
3 { (No. 26)	1.0030	0.0123	1.20}	
4 N.B.S. magnetite (No. 29a)	1.0079	0.0066	0.66	0.62

RECOVERY OF 2,2'-BIPYRIDINE

In view of the rather considerable cost of the complexing agent, it is necessary to devise a simple and rapid scheme for recovering a high percentage of the 2,2'-bipyridine. Indeed, it appears that 1,10-phenanthroline was used to mask iron in a similar determination but that the method was discarded because of the prohibitive cost when the complexing agent was not recovered (11).

It was found that the 2,2'-bipyridine ferrous complex in the filtrate from the alumina precipitation could be decomposed by rendering the filtrate strongly alkaline with sodium hydroxide and heating. When the solution was boiled, the 2,2'-bipyridine could easily be steam-distilled from the decomposition mixture.

When the residue, which contained about 20 grams of 2,2'-bipyridine, had collected, it was allowed to evaporate for several days at room temperature to remove the alcohol which it contained. It was then rendered alkaline with about 100 ml. of 30% sodium hydroxide solution and steam-distilled. The 2,2'-bipyridine soon begins to crystallize in the ammoniacal distillate. If the condenser tube becomes plugged with crystals, it can be

Table V. Recovery of 2,2′-Bipyridine

| Run | 2,2′-Bipyridine | | Recovery % | Remarks |
	Taken Grams	Recovered Grams		
1	3.0	2.5	83	
2	28.0	26.1	93.2	NaHSO₃ and N₂ used
3	21.0	19.4	92.5	NaHSO₃ used
4	21.0	19.0	90.4	NaHSO₃ used
5	21.0	18.9	89.9	NaHSO₃ used

opened by temporarily shutting off the flow of water through the condenser jacket. The addition of sodium bisulfite (about 5 grams for each 20 grams of 2,2′-bipyridine) improves the recovery of the bipyridine. The use of an atmosphere of nitrogen does not sufficiently increase the yield to offset its inconvenience. Snow-white crystals of 2,2′-bipyridine (melting point 69–70° C.) separate from the distillate and are removed by filtration and air-dried. The mother liquor is saturated with bipyridine and should be just acidified with hydrochloric acid and reduced to about one tenth its original volume. It is then added to the next batch for recovery.

Data on the recovery of 2,2′-bipyridine are given in Table V. Experiments with the ferrous complexes of 1,10-phenanthroline

and its 5-methyl and 5-nitro derivatives show that the phenanthrolines can be recovered by the destruction of the complex with hot sodium hydroxide solution. Because these phenanthrolines cannot be satisfactorily steam-distilled, they are extracted with hot benzene and purified by crystallization. Yields of about 80% may be obtained.

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Particle Size Determinations with Electron Microscopes

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Important practical errors inherent in the methods of electron microscopy and how to minimize them, and procedures for securing semiquantitative data from electron micrographs, are discussed in sufficient detail to emphasize factors that have been found from actual experiment most important for accurate, routine counting procedures. If the precautions described are taken and the methods are followed, reproducibility of results within better than 5% is to be expected. High reliance can be placed on the data, and one is justified in using them industrially in process control. An absolute accuracy of much better than 90% is achieved. The precautions are applicable to all fields of electron microscopy and the experimental procedures and statistical methods to any measurement of particle sizes, where the word "particle" is used in the broad sense of "the thing measured for statistical treatment."

THIS paper is presented following requests for a factual discussion that would benefit both those already attempting accurate particle size determinations with electron microscopes and those just beginning the process. The techniques and procedures are not new but they constitute a useful working set of instructions.

The importance of the subject to electron microscopy and its necessarily close alignment with it are very apparent to one who is not content with qualitative results alone but desires some type of quantitative approach. Statistical methods are only semiquantitative but observations may be drawn from them in the form of numbers that can be correlated with other significant specimen variables. Electron microscopy investigations involve two steps: (1) qualitative examination of specimens by broad visual and photographic study, and (2) quantitative study of electron micrographs of samples which are made in controlled experiments often under conditions suggested from the observations of the first step. Because the second is often neglected as being too tedious, maximum advantage of the use of electron microscopes is not always achieved.

This present treatment omits almost completely the problems of proper specimen preparation and deals with two major subjects: (1) the important practical errors inherent in the methods of electron microscopy and how to minimize them, and (2) the procedures for securing semiquantitative results from electron micrographs. The discussion is illustrated chiefly by investigations of polyvinyl acetate emulsions with references to other bio-

logical and industrial samples. The use of the word "particle" in this paper is in the broad sense of "the thing measured for statistical treatment." The procedures apply to particulate materials, and to specimens in general where there are measurable repeating units or structures.

The word "particle" has little practical significance unless its meaning is rigorously defined. Once its definition has been decided upon for a problem, the plates must be counted with care, and all interpretation must be based upon it. If these things are not done, the work has less than maximum significance and it is difficult for others, especially in publication, to evaluate and interpret work in the particle size field.

When the precautions described are taken and the methods outlined here are followed, a reproducibility of results with a variation of 5% can be expected. It is difficult to estimate final accuracy. It has been found that one is justified in placing high reliance upon data secured from these methods, and that these data can be used with good effect in industrial control. It is felt that much better than 10% accuracy is usually reached.

Therefore, justification for the use of these methods and precautions in particle size work with the electron microscope is found in the accuracy and usefulness of the data so obtained and in its agreement with observations made from other sources.

MOUNTING PROCEDURES

Particle distribution and shape may be changed significantly by the mounting procedures. For example, semiliquid droplets

tend to flatten on a film, whereas in a filmless preparation the same effect will not occur; evaporation or contamination may occur in one but not in another type of mounting; particles suspended in liquids are likely to be different than if taken from aerosols; and ground materials may have particle properties at variance with unground samples. In order to be certain of interpretation and reproducibility of results, it would appear advantageous not only to standardize all methods rigorously but also to handle and manipulate samples as little as possible, and to examine them in their naturally occurring state. In general, materials that are employed or occur naturally in a dry state should be examined that way; and if they are used or occur in liquid suspension, they should be so mounted whenever practically possible. A particularly useful method for mounting aerosols as they occur normally in the air involves the use of the the thermal precipitator. A discussion of this apparatus for preparing specimens for electron microscopy is given by Watson (8).

At least two completely different methods of specimen mounting should be used if there is any doubt as to the interpretation of "what a particle is" in a specimen, because a second method of preparation will often dispel this doubt. In this connection, the combination of a dry, atomized specimen with a mulled (7) wet sample is useful. The mulled sample will often give a decreased value of mean size because the mulling tends to break up the larger aggregates and the larger particles. This double mounting procedure is particularly important if the measured quantity is less than 200 Å. in diameter, and is a necessary technique where extent of aggregation is unknown or particle shape is not uniform.

Usually considerable experimentation is necessary to yield a specimen that will give a clear electron micrograph, a reproducible result for the sample, and in the case of particulate samples, a good dispersion.

Just what is to be meant by "a good dispersion" is also subject to the needs of the operator and the properties of the specimen or of the end product in which the specimen may play a part. The measurement of aggregate properties is often more important than the detection of single-particle characteristics. The aggregates in some carbon blacks used in the rubber compounding industry, for example, are known to go through the processes completely with little or no change in properties. In other words, in industrial processes where particulate materials are used as component parts of a final end product, it is the manner in which these occur in the product which is important to the electron microscopist. For this reason microtome sectioning methods are being developed in electron microscopy for many types of sample. A discussion is included below concerning the study of aggregates by "chain diameter" methods. This paper deals with particles in the broad sense and the arguments apply equally to aggregates and to their component parts.

In particle counting studies with electron microscopes, study of two general types of problem may be useful. The first involves the measurement of the absolute sizes of the ultimate, discrete units, a process that usually necessitates considerable experimentation with mounting and specimen examination techniques before it is certain that the desired results are being achieved. The second involves comparative studies where the ultimate particle properties are not needed so much as are comparative data from a series of samples mounted and examined under standardized conditions.

In both cases the data that are secured will be reliable if they are gathered according to the methods suggested in this paper. In the first, however, it is more important to have the material particularly well dispersed and representative in all locations; but in the second, as-long as the procedures are well standardized, the mounting methods are less significant. In both, however, it is necessary to chose the fields by some random technique, and to count and measure the particles according to a standard definition.

CONDITIONS AFFECTING MEASUREMENTS IN ELECTRON MICROGRAPHS

Resolution. For accuracy in particle measurements, it is reasonable to demand that the resolution be sufficient to render visible the smallest particles of the dispersion. This may be less than the distance resolvable practically by an electron microscope, but the general rule is worth applying, that an electron microscope should be kept in a condition of maximum efficiency from the resolution point of view. Maximum resolution is aimed at for all electron micrographs, if for no other reason, because lack of clarity obscures much important information pertinent to one's problem. One effect of lack of resolution in electron microscopy is to increase mean particle diameters by either screening the small particles or broadening the particle diameters in the image. Without sufficient resolution, the ultimate particle nature may go completely undetected and the microscopist continue to be unaware of its existence or properties. Advantages of good resolution are also obvious when one considers the greater ease and accuracy of counting sharp micrographs where eyestrain and interpretation difficulties are reduced.

The following general rules of procedure have been found to be useful in routine work: (1) frequent servicing of the instrument by a single, trained person (the word "servicing" here signifies the alignment procedures but is meant chiefly to indicate thorough column-cleaning techniques), (2) use of a self-biasing (6) electron gun, (3) use of filmless specimens or the thinnest possible films, (4) use of low angular aperture on the high side of condenser current, (5) complete elimination of "dirt" and contamination from the inside of the column, and (6) reasonable alignment of the electron optical system with special attention to the gun and care of voltage alignment.

If we assume optimum microscope performance as regards circuit functioning and instrument operation and construction, there are still several effects which, if present, will contribute to a rapidly decreasing resolving power. No attempt is made here to describe all the factors which can affect resolution, but only those which have been found to be important for accuracy in routine particle work and which can be mostly eliminated by reasonable care.

Vibration is a particularly frequent cause of poor resolution and may go undetected. Large vibrations visible to the eye on the microscope screen are, of course, serious, but usually their source can be traced and eliminated. They are not so dangerous, therefore, as those that are small enough to escape direct observation but great enough to spoil good resolution. Electron microscopes should be set upon well-constructed floors or special mountings, preferably though not necessarily in the basement of buildings distant from sources of major vibration. The pumps should be installed upon damped supports and walking near or leaning upon an instrument during an exposure should be discouraged. Vigorous "crackling" of the diffusion pump oil and shutter movement are known to shake some specimens sufficiently to spoil exposures for proper counting purposes. To provide a more stable specimen support, it is recommended that the object holder be lengthened just enough to touch the top of the objective pole piece. However, if this procedure is followed, its effect upon instrument magnification should be carefully studied. This arrangement gives support at two locations and although good control of the object movement is lost, this is not too serious in particle size determinations because micrographs must be taken at random for reproducible and reliable results.

Extraneous variable magnetic fields entering the instrument in unshielded or only partially shielded locations are often the unsuspected reasons for poor resolution. Usually their effect is to introduce a unidirectional distortion into the image. These may come from continuous sources like near-by power lines or from discontinuous ones such as neighboring elevators. In either case the fields are likely to spoil the image by a considerable amount. Fields as low as 0.0015 gauss are sufficient to shift the image a

distance of about 0.1 micron and produce a diffuse edge of the order of 0.2 micron on the side of the image. Recently, when trouble was traced to extraneous fields from a power line, it was discovered that an edge of about 160 Å. was being introduced. In this case it was reduced to an almost negligible amount by use of the shielding provided between the objective and projector lenses on the E.M.U. instruments (Electron microscope universal, Radio Corporation of America, Camden, N. J.). Therefore, it is recommended that this shielding be used at all times and that in extreme cases an additional cylinder of shielding metal be placed between these lenses. Experimental evidence suggests that varying fields of the order of 10^{-4} or 10^{-5} gauss are able to affect the image contours.

In the author's experience, if one requires accurate routine particle work, routine cleaning of the column is essential. About 2 hours a week and other times as occasion may demand are set aside for servicing the instrument.

Of particular importance for cleaning are the gun, the anode, the condenser aperture, and the objective pole piece. Orange sticks cut to the necessary sizes, finest jewelers' rouge, benzene, and cotton batting are standard equipment. The edges of all metal parts which the beam approaches are rubbed lightly, preferably by spinning the sticks covered with batting and rouge until all polymer deposited by the beam has been removed. Residue rouge powder is completely taken up by using successive applications of clean benzene on cotton. Any particles of dust or pieces of lint visible under a ×10 ocular are undesirable and are removed.

Contrast. Closely akin to the need for resolution is the need for sufficient contrast, especially with specimens of atomically lighter elements and smaller particle dimensions.

The most suitable choices of plates, developing methods, exposure times, and intensities are dictated by experience and available data on these subjects.

As a practical example: Kodak D-72 developer has been found useful when used with Eastman medium or contrasty lantern slides. Intensities and exposure times are regulated by experience to effect a 3-minute development period. For ease in the counting procedures, slightly underexposed plates are best. It has been found that Ilford contrasty special lantern slides are comparably somewhat faster for electrons than the Kodak contrasty and are useful where the increased speed is an advantage.

In order to achieve good contrast, it is generally required first to apply the procedures for best resolution. For routine electron microscopy, the use of suitable objective apertures for increasing contrast is well known and easily applied. On the other hand, their use for improving resolution is very critical and in most cases unwarranted. It is an advantage, however, to be able to use a clean diaphragm of fairly large diameter, useless as far as resolution improvement is concerned, for low contrast specimens. Contamination under electron bombardment or careless handling is likely to render them useless in a few days to a week, but replacement is a simple procedure in the E.M.U. instrument. The objective diaphragms provided for these microscope models can be cleaned three or four times for re-use by careful etching in 30% nitric acid. Most techniques for cleaning the very small apertures without enlarging or spoiling them are impractical and unsatisfactory. The objective aperture assembly recently suggested by Hall (4) would appear to be of great convenience and application.

Distortion. Distortion can affect particle measurements very materially, introducing errors as large as 40% or more under some circumstances (5). To minimize, although not to eliminate its effect, two rules are applied in particle work: (1) Take micrographs near or at the high end of projector current regardless of the projector pole-piece configuration, and (2) on any exposure use only a central circular area of about 2.5-cm. (1 inch) diameter for counting. These two procedures cut down on the magnitude of the error but do not eliminate it. The investigator should realize this and make some attempt to estimate the residual error for its possible influence upon his results.

Focus. The effect of focus upon image contours (6) may influence particle size. If fringes are present, the location of the geometric edge is masked and errors in particle dimensions may be introduced. For slightly underfocused images, the geometric edge is situated just inside the brightest fringe or just outside the darkest one. In focused images the fringes are not present and there is no confusion. For overfocused images, the geometric edge is close to the center of the darkest fringe surrounding the image of each particle. These rules apply to the printed positives not to the negatives. The fringes are observed only when the instrument is operated with a sufficiently small angle of illumination and more often with a biased than an unbiased electron gun.

Magnification. A suitable magnification for a particular specimen is discovered by experience and experimentation with that specimen. With Shawinigan carbon black, for example, where the mean particle size is of the order of 490, the standard deviation is 270 and the particle diameters range through 50 to 2000 Å., a plate magnification of about ×10,000 is satisfactory. Some polyvinyl acetate emulsions of mean diameter of the order of 0.3 micron are most effectively micrographed at about ×5000, while others with extremely large particle sizes, say 1 micron, are taken at about ×1000. In each case, however, the rules for minimum distortion are applied in micrographing and counting the samples.

The plates are taken at magnifications which give a practical number of particles per exposure, are most convenient for optical projection later on, and will render visible the smallest particles at the final magnification.

Electron microscopes are checked regularly for reproducibility of magnification calibration. Where extreme care is required or there is any doubt of the constancy in magnification from specimen to specimen (as when the screens are burred or bent), one exposure of each plate is reserved for the grating replica. The shadow-cast replicas are very useful for accurate routine calibration.

A number of experiments have compared particle size data secured from exposures of a particular field taken at different plate magnifications, when counted at the same projected magnification and when counted at different projected magnifications. The same individual particles were measured from each exposure. General observations from the study are that the mean tends to be less from exposures of lower plate magnification counted at the same projected magnification and from exposures taken at the same magnification but counted at a lower projected magnification. The results are often contradictory, and it is concluded that for the ranges studied the variations in the mean are not significant. The range of instrument magnification was ×13,600 to ×3,540 and the two projected magnifications were ×200,000 and ×100,000. With more extensive ranges, significant variations might be demonstrated.

The use of electron microscopes at low magnifications (less than ×1000) is a neglected field, although there are references (2) to it. By comparative studies at a whole range of magnifications, the gap in interpretation between light and electron microscopy can be most efficiently bridged, and the difficulties of nontechnical people when confronted with electron micrographs can be more easily resolved.

Specimen Changes under Bombardment in Vacuum. In this section are discussed some of the effects of electron bombardment and instrument vacuum upon specimens and in particular upon particle size determinations.

In the first place, some materials tend to evaporate in the vacuum of the instrument. This is accelerated if the sample is bombarded, especially at high intensities. The effect may take the form of direct sublimation as with sulfur and naphthalene, or the sample may vaporize after melting.

Those which melt are almost always present as large masses capable of absorbing sufficient energy; the smaller particles of a dispersion are not melted. Particles thus affected are changed
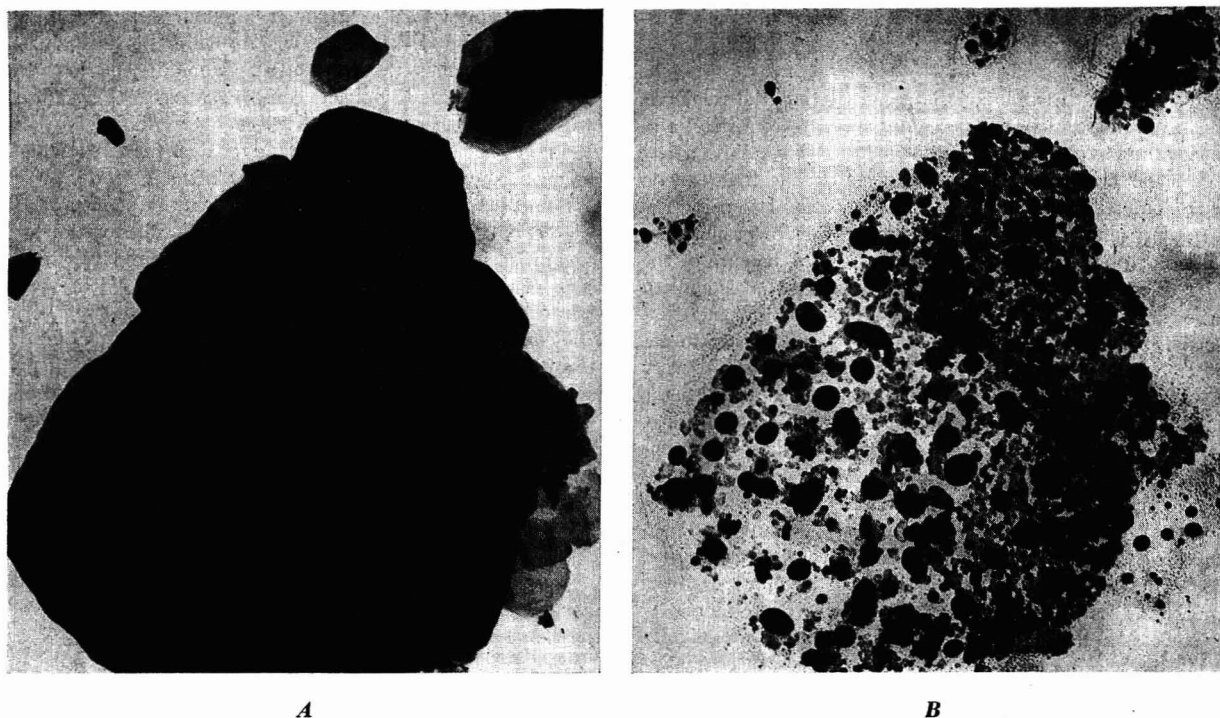
Figure 1.   Electron Micrographs (× 15,000)

A.   Particle-aggregate of tetracopper calcium oxychloride taken at low intensity with little bombardment
B.   Same field as in A after bombardment at high intensity

from pieces of indefinite shape into large round units. This has been observed to happen even with very refractory materials such as titanium dioxide and is most often observed with a biased focused gun where the beam is more concentrated.

Some samples when bombarded evaporate to deposit in a cooler location elsewhere on the supporting film, with appearance unlike that of the original. Often in place of one large unit a whole distribution of small particles is observed. An example of this is seen in Figure 1, A and B. Figure 1, A, shows a crystal of tetracopper calcium oxychloride taken at very low intensity. As the intensity was raised, the hitherto structureless crystalline groups developed a grainy appearance and at a higher intensity the original form was lost completely to give that in Figure 1, B. The outline of the original group remains in the film. Therefore, if a specimen is bombarded carelessly at high intensity (the beam not necessarily focused) pseudo-structures or particle characteristics are likely to be introduced and interpreted incorrectly from electron micrographs.

If high intensities are used indiscriminately, two other artifacts may be present. The specimens, particularly those of biology and medicine, may char; or they may contaminate to increase particle size very materially. Contamination has been discussed fully by Watson (9) and a broad description is unnecessary here. Errors up to several hundred per cent in mean particle size may be introduced according to operating conditions.

The errors due to electron bombardment may be minimized or eliminated if the specimen is subject first to low intensity, so that any change can be observed by the operator as the intensity is raised and micrographs can be taken where the effects do not occur. The errors introduced by vacuum are more difficult to determine and eliminate.

Use of a Biased Electron Gun. In the author's experience the advantages to be gained by using this type of gun outweigh the disadvantages and, once the microscope is set up, it is a simple matter to adapt the gun at a moment's notice for use as an unbiased one. Hence, the advantages of both are available to the operator. With it, it seems easier to achieve routinely good

plates—i.e., those that are usable at optical magnifications of ×20 or more. This is due partly to the increased intensity which allows more accurate focusing, also to improved instrument alignment with a smaller numerical aperture; less care has to be taken to secure better resolution. This is, of course, very important in particle measuring work where a comparatively large number of uniformly good micrographs are required in a short time. Biased electron sources are now available from Vibration Systems, Inc., 1040 West Fort St., Detroit, Mich.

However, greater care has to be taken when the gun is used, that the greatly increased intensity does not introduce the errors of contamination, electrostatic charge effects, specimen heating, evaporation, or melting. In addition, filament life is decreased and metal parts of the microscope become contaminated more rapidly. The author has yet to find a sample that could not be micrographed satisfactorily using a biased gun.

PROCEDURES IN PARTICLE COUNTING

If the above precautions have been observed adequately and usable plates are availble for counting, the first questions with which one is confronted are: how many plates should be taken and how many particles is it necessary to count? (Throughout this discussion "count" and "measure" are used interchangeably with their combined meanings.) A good criterion to be followed in answering this is: take the number of plates that will give enough particles to demonstrate a reproducibility of the results to within 5% from specimen to specimen of the same sample. This percentage is an indication only of the reproducibility and not of the accuracy, but it is axiomatic that the accuracy of results will be less if the reproducibility is not reliable. The number of plates to be taken will vary with different types of samples and is dependent to a large extent upon the uniformity of the thing being measured. In general, the smaller the standard deviation the smaller the number of particles that must be counted. An example may be helpful. Good results are obtained with Shawinigan black if at least a thousand particles are counted from four different plates per sample. This means that twenty different

fields are examined. It is important to note here that the micrographs are taken completely at random: choice must play no part in the process.

Throughout this discussion, it is assumed that the reader is anxious to secure results that are most accurate routinely, and that he is willing to go to some pains to achieve this. With a new specimen type about which the investigator has little or no knowledge, the results are checked from plate to plate using the same sample preparation, and from preparation to preparation upon different plates. Only in this way can one be sure of the methods. The time is not lost, for coupled with what is learned about the sample and the techniques, there is the other fact that all the counts for the material can now be put together to get what is called the "composite" results, which are usually very reliable. When information has been secured concerning the methods to be applied in order to secure good statistical data, routine work is possible, quality control charts may be drawn for a product, and trends and graphs plotted in studies of the variations of particle sizes with other important properties of a substance or the process by which it is made.

Before the actual counting begins it must be clearly understood by those counting just what property of the specimen is to be measured, and this choice must be followed rigorously thereafter if comparative results and calculations are to have any significance. In particle work one usually has a choice of three quantities for measurement: the long, the short, or the mean diameter. In special cases where the shape is recognizable, two or more dimensions may be important. The long diameter is used most conveniently in measurement and in later calculations, especially where the shape of the particles is variable. In measurements of structure, special definitions of the thing to be measured have to be made but the results can still be handled statistically. Methods for measuring aggregates are discussed elsewhere in this paper. When ultimate particles are measured, only those units of which at least half of the circumference is visible should be counted. To make this last statement completely practical, one may need on occasion to work with the mounting procedures until preparations suited for representative results are secured. In special cases recourse may be had to stereoscopic electron microscopy for aid in interpretation.

The plates are projected for observation upon a screen at convenient magnifications which permit the easiest calculations—i.e., $\times 200,000$, $\times 100,000$, or $\times 50,000$. (The Spencer Delineascope, model MK, is excellent for this work. An adapter which will carry a 10 by 2 in. plate has to be made to use with it. The projector will handle optical magnifications from $\times 10$ to $\times 35$ conveniently.) Measurements are made with a ruler in millimeters, which at these magnifications result in ranges of 50, 100, and 200 Å., respectively. (The rulers are transparent for most convenient work. Transparent rulers with better than average accuracy are obtainable from C-Thru Ruler Company, Hartford, Conn. The scale is held in these rulers between two thin flats of plastic. This prevents wearing of the scale as the ruler is rubbed continually against the screen in the counting procedures.) The screen is of rigorous construction, made of smooth wood, and painted a flat white. It is fastened firmly to a wall of the projection room, and squares 6 inches to the side are drawn upon it, to aid in orienting oneself during the counting procedures. To make precautions against distortion effective, a circle of appropriate size is drawn on the screen and only those particles falling within it are measured. One person alone may carry out the counting, using a ruler with one hand and operating a counting device with the other, or two people can cooperate. The projector is mounted upon a table which is about 5.5 feet high and stands on casters, so that it can be moved readily to change the magnification. The table should be well constructed and have a top with dimensions approximately 1 by 2 feet. The body of this table can be divided into suitable chambers convenient for storing plates.

The process is likely to be tedious and it is advisable to have large scale counting done only in the morning with fre-

quent rest intervals. Fatigue or boredom will invariably lead to inaccurate results. It is not wise to have two individuals doing the counting unless their mutual reproducibility has been checked. One should strive in particle counting work to take micrographs with a little less contrast and plate blackening than is usually thought to be ideal. Too light and too dark plates are equally bad as regards the comfort of the counter in the matter of eyestrain.

Some laboratories do not avail themselves of projection of plates, but prefer to print each exposure for observation at higher magnifications, or to examine the plates themselves with an ocular. These methods have their advantages, but it is very worth while to couple them with plate projection, not only because of the convenience but because it allows the whole micrograph to be examined at one time and no detail is lost as it is in printing. Suitable fields can be picked out for printing later, and one does not have to wait for the time-absorbing photographic processes to be completed before being able to examine the plates. Higher magnifications can be used in projection than for photographic printing. One must remember, however, that the projected image is a negative and not a positive.

There should be a constant attempt on the part of the microscopist to develop and use shortened methods if the required accuracy will allow it.

STATISTICAL METHODS

The following remarks apply wherever there is a distribution curve to be considered. At the present state of the science, it is hardly practical to attempt to draw a distribution curve for samples of mean diameter less than 100 Å. With such fine samples, micrographs of high resolution and the measurement of a few clear particles are probably sufficient to give the mean diameter.

In electron microscopy where such wide ranges of sizes are resolvable, it is often necessary with samples of extreme deviation
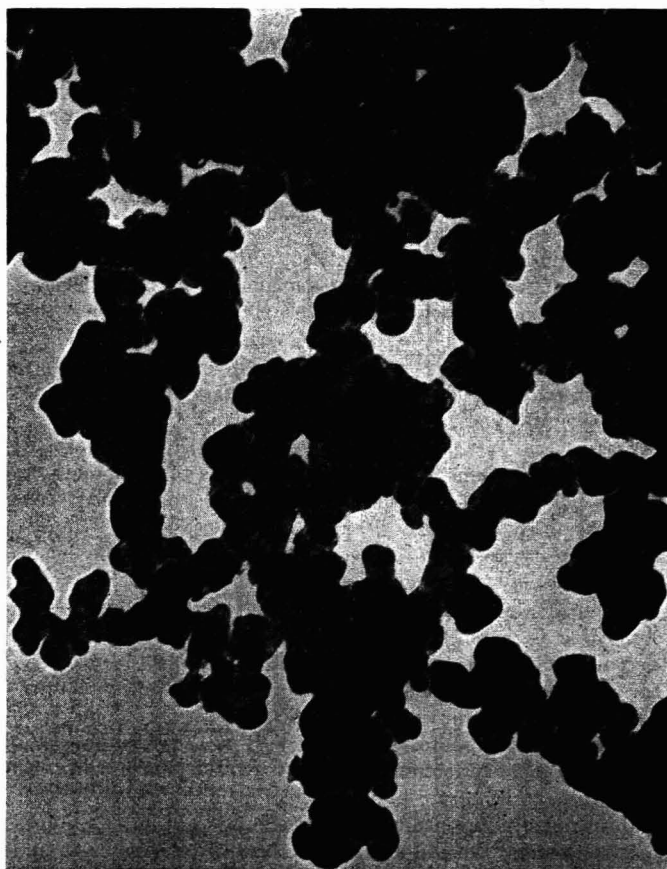

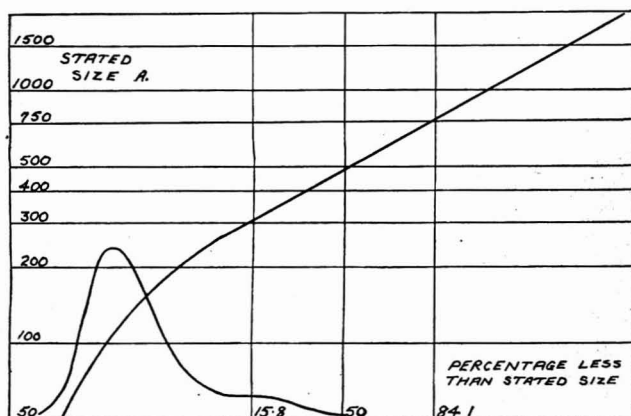Figure 2. Shawinigan Acetylene Black ($\times 100,000$)

Figure 3. Distribution of Particle Sizes in Shawinigan Black

to define the range to be studied. It may even be necessary, practically, to examine several such ranges separately. No rules can be given for such procedures, which depend so much upon individual needs.

By far the greater number of distributions in nature are asymmetric with their peak displaced most often toward the small sizes, and usually these yield straight lines when plotted as cumulative per cent greater or less than stated size along the abscissa against stated size along the ordinate upon logarithmic probability graph paper. [Logarithmic probability paper and arithmetic probability paper are vailable from the Codex Book Co., Inc., Norwood, Mass. The special grids were developed by Hazen. Some discussion of their use is given by Dalla Valle (3).] For several reasons to be found in the following paragraphs, it is more convenient to use this curve than the more usual types.

The geometric mean is read directly from the curve where it cuts the ordinate drawn from the 50% position. The geometric standard deviation is found by using the relation:

$$\text{Standard deviation} = \frac{84.13\% \text{ size}}{50\% \text{ size}} = \frac{50\% \text{ size}}{15.87\% \text{ size}}$$

Thus, the statistical constants may be taken very quickly from the graph, much tedious calculation is saved, and the graphs themselves are easily drawn. For comparison purposes several distributions may be plotted without confusion upon one sheet. One further advantage over other methods of plotting comes from the fact that it is easier to draw a line accurately through the average of a number of points than to try to trace a distribution curve of the usual type. In addition, straight lines are more accurately reproducible.

In these plots discrepancies from straight lines are often observed. One of the most usual is a tendency for the curve to be slightly concave downwards. Such distributions may be approaching the symmetrical condition, although in practice symmetric dispersions also are often found to give good straight lines on logarithmic probability paper, contrary to the predictions of theory. The concavity may also be a result of a tendency toward a double dispersion in the sample, or of an insufficiency in the number of particles which have been counted. It is usually possible to draw the concave curves as two straight lines meeting at a point break. If there is a very definite double dispersion, there will again be two straight lines, this time not meeting at a point but in a step break in the curve. The occurrence of such a step is good evidence of a double distribution. These phenomena are illustrated in examples that follow. The extremes of the lines are rarely straight because of the tendency to get unrepresentative counts at both the very small and the very large, and because the distributions are not asymptotic at the extremes. Such discrepancies do not affect the results to a significant extent. In general, the more asymmetric the distribution, the better the line, and for

samples where there is no demonstrable peak at all (hyperbolic curves) the best lines seem to be secured.

If the distribution is symmetric, the results are plotted upon arithmetic probability paper to give theoretically again a straight line. In this case the plotting is done as before, except that the ordinate scale is now an arithmetic one. However, relatively few examples give satisfactory straight lines on this paper. There seems to be a fundamental discrepancy in the theory, for where the theory calls for a straight line when a symmetric distribution is plotted arithmetically, this does not always occur in practice and, in general, regardless of the extent of symmetry the best lines are secured in the geometric graph.

The arithmetic mean may be read off in the same manner as previously, and the arithmetic standard deviation is taken from the relation:

$$\text{Standard deviation} = 84.13\% \text{ size} - 50\% \text{ size}$$

or

$$= 50\% \text{ size} - 15.87\% \text{ size}$$

The use of probability graph papers is by no means restricted to problems of particle size alone, but may be used for describing and studying the characteristics of any problem where curves with distribution shape are involved.

CALCULATION OF SPECIFIC SURFACES

The mean particle diameter as such is not always the most important one, but the mean surface or volume diameters are likely to be much more worth consideration practically. This is a well-recognized fact and yet most electron microscope articles on particle size mention only the mean diameter. It should be otherwise, for whereas in light microscopy the shape factors and surface characteristics of particles are usually invisible except in the very large fractions, these properties are visible in many electron micrographs and universal assumptions of sphericity do not have to be made. Both the mean surface and volume diameters are derived readily from particle size data, using logarithmic probability paper if the appropriate constants for particle shape are employed. The use of probability paper is discussed here only for problems involving particle size, as the arguments are analogous for the other cases.

Electron microscope determinations of particle dimensions usually give values about an order less than other methods, including those of light microscopy, but if proper considerations are taken of shape and the particles are not porous, gocd agreement with the methods of nitrogen adsorption can be secured in the determination of specific surfaces from particle distribution considerations. Certainly, if the properties of the finest fractions of a material are important, no method other than electron microscopy can give direct information about them.

In the well-known formula for specific surface, assuming universal sphericity of particle shape,

$$S = \frac{6 \times 10^4}{p \times d} \text{ square meters per gram}$$

where p = the true density in grams per cubic centimeter, and
d = the mean longest diameter of the ultimate particles in Ångström units.

The use of this formula gives an increasing error as the value of the standard deviation increases. If the spread is sufficient to introduce an appreciable error, the mean surface diameter must be used instead of d.

Electron micrographs give observations of particle shape which are not available from other sources and thus allow corrections to be made to specific surface values for departures from the spherical. If there is a shape distribution over a sample, a new property called the mean shape (10) is introduced. With this taken as an approximation to the true shape, constants k and v are calculated and applied to the original value of S.
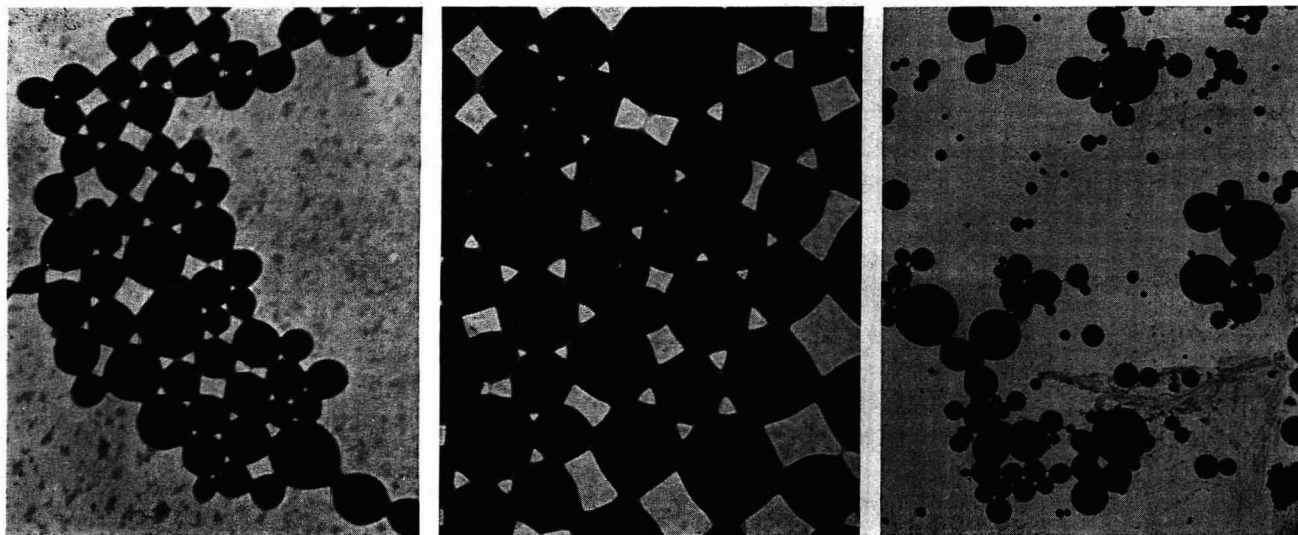
Figure 4. Polyvinyl Acetate Emulsion

Left. Basis of A and A', Figure 5 (19,000). Center. Basis of B and B', Figure 5 (16,000). Right. Basis of C and C', Figure 5 (1600).

$$k = \frac{\text{surface area of true shape}}{\text{surface area of sphere}}$$

$$v = \frac{\text{volume of sphere}}{\text{volume of true shape}}$$

$S' = kvS$ = value of the specific surface for the true shape

A particular application of this comes in the electron microscopy of large particles which have sufficient size in their large dimension at least to be readily observed and counted under a light microscope, but in which even considerable variations in shape would not be resolved except in an electron microscope.

TWO SPECIAL TECHNIQUES

Two other statistical techniques which are adaptable to the purposes of electron microscopy are called chain counting and squaring. The first is used in attempts to measure semiquantitatively that illusory property known as structure in some particulate materials, and the second is used to ascribe a number to a mixture significant for describing one or more of its components.

Chain Counting. In chain counting the maximum distances across aggregates are measured and treated statistically to give the mean chain diameter. It is found that the value of this chain diameter is a function of the extent-of-structure and to some extent is a measure of it. In observations of several carbon blacks it is found to be characteristic of the particle black. The specimens must be prepared by well-controlled standardized methods which are kept constant for each sample compared in a series. Micrographs are generally taken at relatively low magnifications, because the aggregates are likely to be large. The method may be used absolutely, but also has definite application in comparative studies of aggregation.

Squaring. If a specimen has two or more components which are recognizably different in electron micrographs, the method of squaring may be useful for securing a number by which the sample may be described. The method is not absolute but has comparative value. In order to measure the squaring value of the sample, plates are set at random in a projector and the number of squares on the screen which contain the least trace of one or other of the materials are counted. Suppose that x squares contain the material looked for and that y squares contain none of it, the squaring value for the material is then calculated as:

$$\frac{x}{x+y} \times 100$$

One example of the usefulness of this method may be taken from the study of catalytic cuprene growths in certain catalysts. The typical cuprene structure is readily distinguishable, and a squaring value which is descriptive of the prevalence of cuprene in the sample can be measured. This value can be plotted in turn against time, or catalytic activity.

EXAMPLES

The following examples are all of cases that involve the measurement of what may be called the ultimate particle size of a sample. Except in one case, as noted, logarithmic probability paper is used and hence the geometric statistical constants are given in the results. In all cases, only those particles are counted for which at least half the circumference is visible. The industrial samples of carbon and polyvinyl acetate emulsions yielded results which were used in actual production problems. The biological specimens of sperm and bacillus are mentioned briefly to emphasize that these methods are applicable in many fields.

Shawinigan Carbon Black. Carbon blacks are particulate materials in which the particles and their shapes can be recognized fairly readily. For some exceptions to this, (10) may be consulted. The particles of Shawinigan black occur in chains and it is said, therefore, to possess structure and can be studied consequently by statistical methods for both particle and chain diameters. Both these techniques have given useful information concerning these characteristics of the material and their correlation with its properties. Figure 2 shows a typical field of Shawinigan black which yields the type of distribution outlined in Figure 3. Both the normal frequency plot and the logarithmic probability graph are drawn for comparison. The thing measured in this example is the longest dimension of the particles and for calculations of surface or volume characteristics the oblate spheroid is chosen as the "mean shape."

The distribution is slightly asymmetric and the plot on logarithmic paper is a good straight line over the major portion of the curve, a concavity downwards entering in the region of the small particles. The tendency toward a double peak is not strong enough to cause a break in the line. The mean diameter is read as 490 and the standard deviation is 270 Å. If the same values are plotted upon arithmetic probability paper, a curve is obtained which deviates even further from a straight line than that on logarithmic paper. It is strongly concave upwards along its whole length.

The data for this particular example are the composite from a large number of experiments done upon many samples. For the over 11,000 particles measured, the numerical figures are given in Table I. These are representative of the simple calculations required for these methods.

Table I. Frequency Distribution of Shawinigan Acetylene Carbon Black

Diameter, Å.	Frequency	Percentage in Range	Percentage Less Than Stated Size
50	7	0.060	0.060
100	62	0.535	0.595
200	369	3.187	3.782
300	1088	9.407	13.189
400	1968	17.007	30.196
500	2255	19.478	49.674
600	1956	16.888	66.562
700	1548	13.472	79.934
800	954	8.241	88.175
900	593	5.122	93.297
1000	336	2.902	96.199
1250	303	2.617	98.816
1500	101	0.873	99.689
1750	27	0.233	99.922
2000	9	0.077	99.999
	11,576	99.999	

Geometric mean diameter 490 Å. $\pm$ <10%
Geometric standard deviation 270 Å.

Total range 50 to 2000 Å.
Approximately 65% of the particles lie between 220 and 760 Å.

Table II. Statistical Constants for Polyvinyl Acetate Emulsion Samples Used as Examples

Sample	Mean Diameter $\pm$, < 10% Microns	Standard Deviation Microns	Total Range Microns
Figure 5, A	0.26	0.06	0.13-0.55
Figure 5, B	0.52	0.16	0.2 -1.2
Figure 5, C	1.13	1.27	0.33-6.33
Figure 6, A	1.45	2.55	0.4 -8.0
Figure 6, B	0.94	0.40	0.4 -2.2
Figure 6, C	3.46	1.14	1.9 -8.0
Figure 8, A	1.66	0.53	0.3 -9.0
Figure 9, A	2.90	1.22	0.8 -7.0

Polyvinyl Acetate Emulsions. Plastic emulsions are excellent electron microscope specimens and a natural field for application of the instrument. They give good contrast micrographs (Figure 4) and possess particle sizes which, while they may enter the regions of the very small, may also trespass on the territory of the light microscope. As such they serve as good test objects for comparing results and interpretation with the two instruments. The particles are distinct spheres and a definition of the thing to be measured is easily made.

The three emulsions represented in Figure 4 are plotted upon logarithmic probability paper in Figure 5 as curves A, B, and C, respectively, and are traced as curves A', B', and C' in the more usual manner. The sharply peaked symmetric curve, A', gives a straight line upon logarithmic probability paper. In comparison with it, the slightly asymmetric curve, B', with a very broad peak also gives a straight line. The most asymmetric curve of the three, C', gives a straight line which is broken in a point toward the large particle sizes. The three logarithmic probability graphs are plotted upon the same sheet with the same abscissa line in Figure 5 in order to demonstrate how this graph paper may be used conveniently to show clearly a comparison of the properties of a number of similar samples. The means may be compared along the ordinate drawn to the 50% position on the abscissa, and the standard deviations may be compared by observations made on the respective slopes of the lines. None of these examples gave as good a line when plotted upon arithmetic probability paper.

Figure 6, A, is an extreme case of what has been called in this paper a step break in a logarithmic plotting. Usually the steps are not so abrupt nor so large as this one but resemble that in Figure 8, A. The usual types of distribution curves have been drawn again for these two examples and both are seen to possess double peaks. When such peaks are recognized, it is doubtful to what extent the mean and the standard deviation values taken from the broken curve have significance. The distribution can be broken mathematically to give two curves, each representing a single peak of the original, and these plotted separately give usable data concerning the sample. Figure 6, B and C, are the two segments of A treated in this way. Presumably, two types of nuclei, or seeding, must have been present during manufacture in order to give a break. Such breaks serve as indications of this effect and of its intensity. The data

for A, B, and C of Figure 6 are schematically traced in Figure 7. Mean values and standard deviations for all the emulsion samples are given in Table II.

Another emulsion sample is represented by B, Figure 8. It is typical of the concave downward type of graph which is often obtained on logarithmic probability paper. This particular distribution cannot be represented as a point break on logarithmic paper but can be so handled on arithmetic paper (Figure 9). The values of the statistical constants for this sample given in Table II are taken from the arithmetic plotting. The sche-
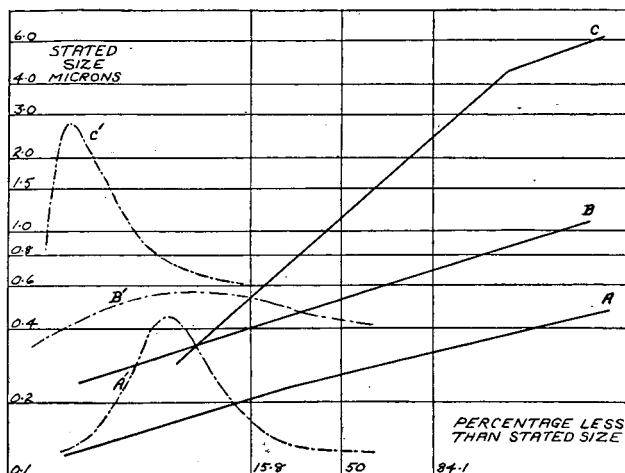

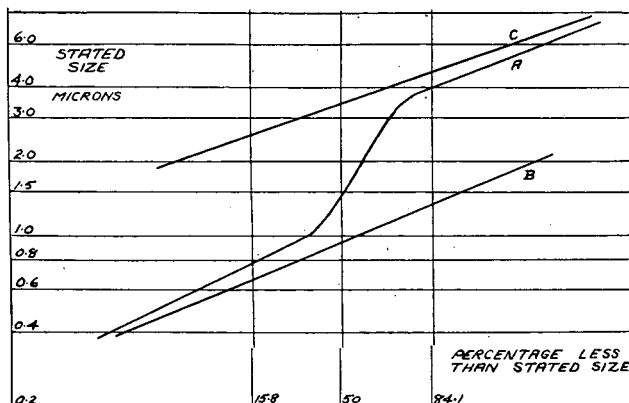**Figure 5. Particle Size Distributions of Emulsion Samples in Figure 4**

Figure 6. Polyvinyl Acetate Emulsion Particle Size Distribution with Double Dispersion Plotted upon Logarithmic Probability Graph Paper

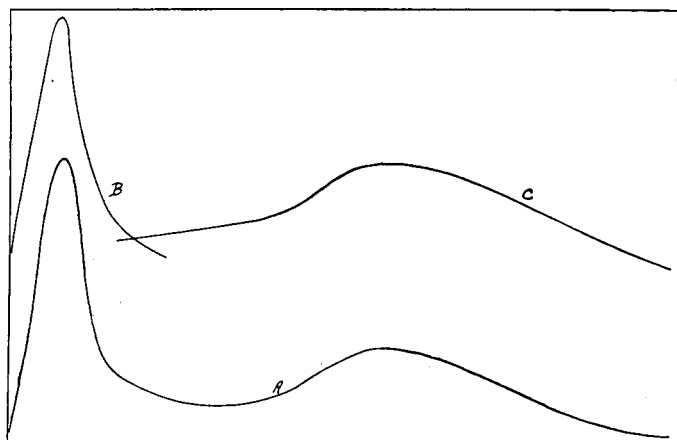A. Whole distribution. B. Small fraction. C. Large fraction

Figure 7. Distributions for Each of Curves in Figure 6

matic tracing of the distribution is shown in Figure 8, *B'*, and in Figure 9. It is broad peaked and slightly asymmetric.

Sperm. The application of these semiquantitative methods to the study of biological and medical specimens has not been exploited to any important extent. It is an approach that may make information available which can be correlated with clinical data.

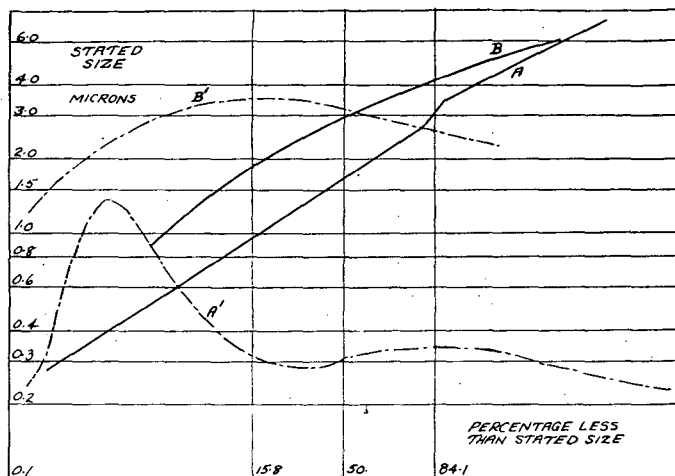As an illustration of the type of thing which can be measured, micrographs were taken of a sperm sample and statistical con-

stants characteristic of the specimen determined by plotting the distribution on arithmetic paper, Figure 10. An almost symmetric distribution gives a straight line. The quantity measured for these particular results is the maximum distance across the heads. There are other characteristics of the bodies which can be treated in the same way and which may be more important for study. The mean of the readings is 2.33 and the standard deviation, 0.45 micron. The total range is 1.25 to 4.0 microns for the sample. Approximately 65% of the individuals are between 1.88 and 2.78 microns in diameter.

Friedlander Bacillus. Likewise, the lengths or the widths of bacilli and viri (*1*) may be significant variables when correlated with clinical data, and the electron microscope offers an accurate method of securing numbers which will describe these characteristics.

A Friedlander bacillus specimen was studied and the results are reproduced in Figure 11. This bacillus is uniform as regards particle sizes, having a standard deviation of 0.42 and a mean of 1.39 microns. The quantity measured in this case is the length of the organism. Logarithmic probability paper gives the best straight line for this case. With these specimens standardization and suitability of mounting and examination procedures are particularly important.

ACKNOWLEDGMENTS

Figure 8. Polyvinyl Acetate Emulsion Particle Sizes Plotted upon Logarithmic Probability Paper

A. Dispersion with a slight step break. *B.* Concavity downward on logarithmic paper. Schematic representation of distributions given in *A'* and *B'*
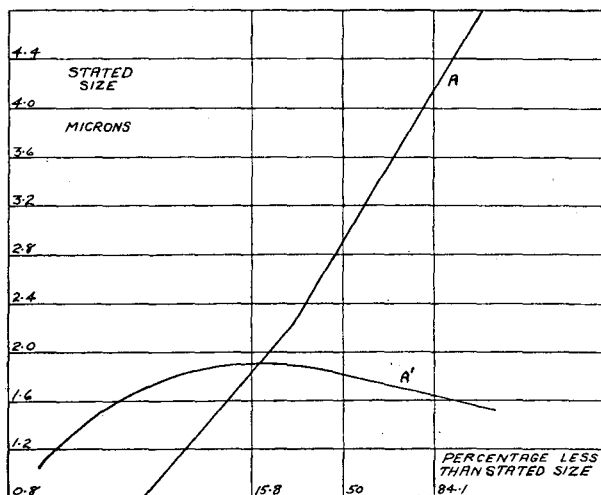
Figure 9. Same Sample as in Figure 8 *B* and *B'*

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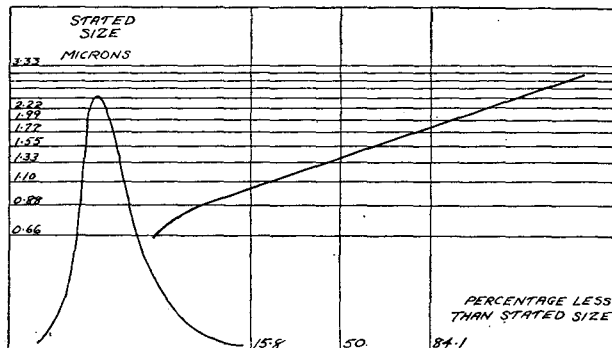**Figure 10. Diameters of Heads of Sperm**

Figure 11. Lengths of Friedlander Bacilli

Amperometric Microtitration of Diamidines

JOHN B. CONN, *Merck & Co., Inc., Rahway, N. J.*

An amperometric titration procedure is based on formation of insoluble di-
amidine alizarinsulfonates, which permits rapid and quantitative estimation of
certain diamidines alone or in simple pharmaceutical preparations. With suit-
able equipment, 5 mg. or less of diamidine salt can be assayed to within ±0.5%.

WITHIN recent years, certain aromatic diamidines have been employed in the treatment of protozoal infections. These compounds belong to the general type

$$-X^- \; H_3\overset{+}{N}-\underset{NH}{\overset{\|}{C}}-\langle \rangle -R-\langle \rangle -\underset{NH}{\overset{\|}{C}}-\overset{+}{N}H_3 X^-$$
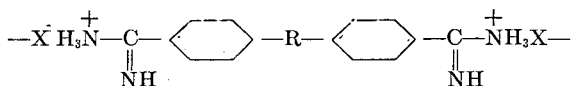
where R may be variously —O—, —CH=CH—, or —O—(CH$_2$)$_n$—O— (*1*). Inasmuch as it is known that the amidino group is subject to hydrolysis to the corresponding amide, with, in this case, loss of protozoicidal activity, it is desirable that some means be devised for the accurate determination of those diamidines which are in general medical use. From the pharmaceutical standpoint the analytical method should be applicable both to purity control and to study of the stability of the preparations under various conditions of sterilization and storage. Devine (*2*) and Fuller (*3, 4*) have described colorimetric procedures for the estimation of diamidines, based on a reaction with glyoxal. These methods, although applicable to diamidines in biological fluids, are not sufficiently accurate for purity specifications. The requirement here is precision rather than universality of conditions under which the method may be applied.

The particular diamidines under consideration were (1) 4,4'-stilbenedicarboxamidine diisethionate (stilbamidine), (2) 4,4'-oxy-dibenzamidine dihydrochloride (phenamidine), (3) *p,p'*-(trimethyl-enedioxy)dibenzamidine dihydrochloride (propamidine), and (4) 4,4'-(pentamethylenedioxy) dibenzamidine dihydrochloride (pentamidine).

It was observed that all gave, in neutral solutions, highly insoluble red alizarinsulfonates. The alizarinsulfonate of phenamidine was consistently obtained in crystalline form, and that of propamidine was so obtained occasionally; the alizarinsulfonates of stilbamidine and pentamidine were microscopically amorphous. Analysis of the well crystallized phenamidine alizarinsulfonate indicated a 1 to 1 molecular composition. Calculated for C$_{28}$H$_{22}$O$_8$N$_4$S: C, 55.10; H, 4.29; N, 9.18. Found: C, 55.33; H, 4.28; N, 9.17. Consequently, one of the phenolic hydroxyls as well as the sulfonic group is involved in the insoluble salt formation—a situation which is further evidenced by the failure of sodium anthraquinone β-sulfonate to give any precipitate with diamidine salts. Attempts were made to utilize the reaction in colorimetric and gravimetric procedures of analysis, but these met with failure. In the first instance,

the precipitates tended to adsorb alizarinsulfonic acid when the reagent was in excess, and in the second instance, peptization of the solids occurred on washing (with the exception of phenamidine alizarinsulfonate).

The conditions of precipitation were such as to indicate the possible utility of an amperometric technique. Alizarinsulfonic acid is polarographically reducible; in 0.1 M phosphate or borate buffer, pH 7, the half-wave potential is −0.67 volt (versus the saturated calomel electrode), and at −0.90 volt a steady diffusion current is reached. When a solution of one of the diamidine salts in neutral buffer was titrated with a solution of sodium alizarinsulfonate, a plot of the diffusion current at −0.90 volt (corrected for dilution) versus volume of reagent resolved into two straight lines intersecting at a 1 to 1 equivalence point. Standardization of the sodium alizarinsulfonate was effected by titration of a sample of diamidine salt whose purity had been established by the technique of solubility analysis. It was found that standard solutions of the reagent could be made up directly, provided that the sodium alizarinsulfonate was pure and thoroughly dried at 100° C. in vacuo.

Apparatus. The polarograph employed was a Leeds & Northrup Electrochemograph. The cell was adapted from that described by Lingane and Laitinen (*5*), with the modification that the dropping electrode compartment was fitted with a stopcock at the bottom for easy drainage. The cell capacity was 10 ml. The microburet was a Rehberg mercury-expulsion type of 0.25-ml. capacity. The entire equipment was housed in a room thermostated at 25° ± 0.2° C.

Reagent. Merck reagent sodium alizarinsulfonate was recrystallized from hot 50% alcohol; the solid was dried in vacuo at 100° C. before use. The salt was dissolved in 0.1 M phosphate or
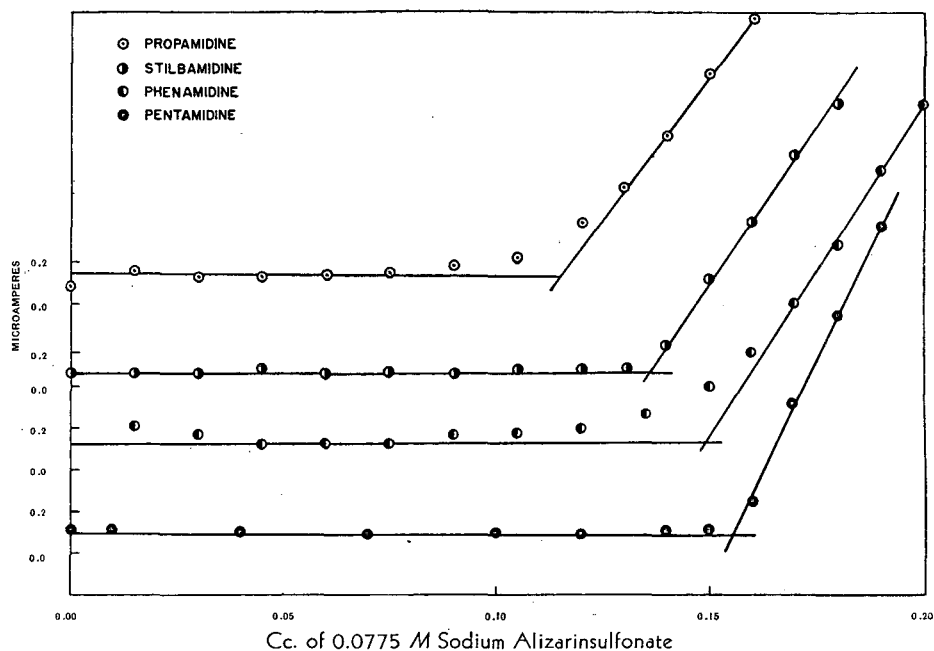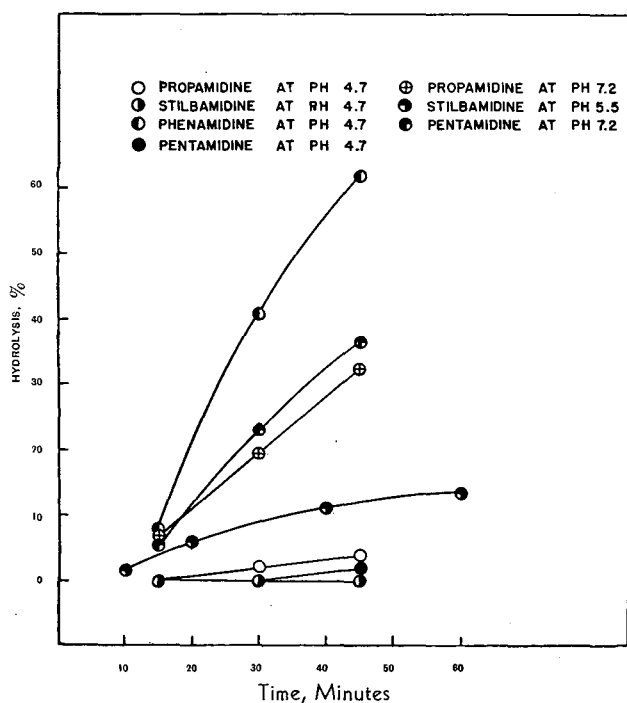

Legend:
⊙ PROPAMIDINE
◑ STILBAMIDINE
◐ PHENAMIDINE
● PENTAMIDINE

MICROAMPERES

Cc. of 0.0775 *M* Sodium Alizarinsulfonate

Figure 1. Titration Graphs

Table I. Comparison of Amperometric Titration and Solubility Analysis Methods

Diamidine Salt	Assay, Per Cent	
	Amperometric titration	Solubility analysis
Stilbamidine diisethionate	100.0	99.7
Stilbamidine diisethionate	99.8	99.5
Phenamidine dihydrochloride	94.3	94.0
Pentamidine dihydrochloride	95.5	96.0

Table II. Reproducibility of Amperometric Titration Assays

Diamidine Salt	Assay, %	Average, %
Stilbamidine diisethionate	99.5	
	100.5	
	99.5	99.8 ± 0.4
Propamidine dihydrochloride	84.5	
	85.3	
	85.0	84.9 ± 0.3
Phenamidine dihydrochloride	99.3	
	99.5	
	100.8	99.9 ± 0.6
Pentamidine dihydrochloride	100.0	
	100.0	
	100.5	100.2 ± 03

O PROPAMIDINE AT PH 4.7   ⊕ PROPAMIDINE AT PH 7.2
◑ STILBAMIDINE AT RH 4.7   ◐ STILBAMIDINE AT PH 5.5
◔ PHENAMIDINE AT PH 4.7   ◕ PENTAMIDINE AT PH 7.2
● PENTAMIDINE AT PH 4.7

Figure 2. Hydrolysis of Diamidines at 120°

borate buffer to about 0.08 M. If the buffer is free from ions which precipitate alizarinsulfonic acid, such as aluminum and iron, the solution is standard as prepared; otherwise it must be standardized against a diamidine salt of known purity (determined, in this case, by the technique of solubility analysis).

Procedure. Six to 10 mg. of the diamidine salt were weighed out on the microbalance and dissolved in 10 ml. of neutral buffer. A 5-ml. aliquot of this solution was transferred to the polarograph cell, the dropping mercury electrode and buret were assembled, and nitrogen was passed through the solution for 5 minutes.

The polarizer was set at −0.90 volt (vs. S.C.E.), the recorder at 5 microamperes. The cell was connected to the recording unit, and after the galvanometer had reached equilibrium, the chart was set in motion until a straight line had been drawn through one or more chart divisions; the chart was stopped, for convenience, on a division. When the zero-point record was completed, 0.01 to 0.02 ml. of alizarinsulfonate solution was added from the buret, nitrogen was passed through for 2 minutes, and the recording procedure was repeated. The cycle of operations was continued

until the diffusion current was increasing linearly with additions of alizarinsulfonate, as shown by the appearance on the chart of three or four steps of equal magnitude. The chart, which provided a permanent record of the titration, was read off, the value of the diffusion current for each addition was corrected for dilution where the corrections became significant, and the usual graph of diffusion current versus volume of reagent was prepared for determination of the end point.

In the case of phenamidine, separation of the crystalline alizarinsulfonate occurred slowly. It was found advisable to add a little of the solid phenamidine alizarinsulfonate to the solution at the start of the titration, so as to saturate it and provide seed crystals. Until the end point was well passed, ample time had to be allowed after each addition of reagent for crystallization of the precipitate; otherwise erroneously high current values were obtained.

DISCUSSION

In Figure 1, typical titration graphs for the four diamidines are plotted. In the cases of stilbamidine and pentamidine, the points show substantially no deviation from linearity in the region of the equivalence point—an evidence of the high insolubility of the precipitates. On the other hand, considerable deviations appear in the same regions of the phenamidine and propamidine graphs; the alizarinsulfonates of these diamidines have measurable solubilities, that of phenamidine alizarinsulfonate being the greater. In addition, the effect of the lag in separation of phenamidine alizarinsulfonate is observable at the beginning of the titration; the initial points tend to be above the line, despite the extra time allowed between addition of sodium alizarinsulfonate and recording the diffusion current.

A comparison of purities established for certain samples of the diamidines by amperometric titration and by solubility analysis is given in Table I. The agreement is seen to be satisfactory, even in the case of phenamidine, the attendant graphing uncertainties of which are apparent in Figure 1. The reproducibility to be expected in the amperometric assay is illustrated by Table II, which lists the results of triplicate assays on samples of the four diamidines, selected at random. The greatest spread in results is, as expected, to be found in the phenamidine data—about 1.5%; the other amidines supply data concordant within an average of ±0.4%. The over-all reproducibility, is taken to be ±0.5%.

Because it is of interest to apply the titrimetric method to study of the stabilities of the diamidines under sterilization conditions, some of the data which have been collected are graphed in Figure 2. Solutions of the diamidines were autoclaved at 120° C. under conditions of pH known to cause hydrolysis of the amidine groups, and sampled from time to time. It is to be expected that hydrolysis should accelerate with increasing pH, as amidine bases are less stable than their salts. Although this is true, there are other structural factors bearing upon the hydrolysis rate, as will be seen by the fact that the amidines fall into three stability groups analogous to their structural groups. Thus phenamidine is highly sensitive to hydrolysis at pH 4.7, propamidine and pentamidine are attacked only slightly, and stilbamidine not at all.

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Microdetermination of Sulfur in Organic Compounds

AL STEYERMARK, ESTHER BASS, AND BELLA LITTMAN

Hoffmann-La Roche, Inc., Nutley, N. J.

A micromethod for determining sulfur is presented which employs the Carius combustion followed by titration of the resulting sulfate with barium chloride. The tetrahydroxyquinone indicator method of Ogg, Willits, and Cooper is used.

THE use of the tetrahydroxyquinone indicator (prepared by W. H. and L. D. Betz, Philadelphia) in the microdetermination of sulfur in organic compounds has been described by Hallett and Kuipers (*2*), Sundberg and Royer (*6*), Alicino (*1*), and Ogg, Willits, and Cooper (*4*). All these authors used the catalytic combustion method to destroy organic material and to convert the organically bound sulfur to sulfate, previous to the titration with barium chloride.

A demonstration by Willits and Ogg in their laboratory convinced the present authors of the value of the illuminated titration stand technique, and they decided to adopt the method in this laboratory. Good results were obtained with sulfanilic acid in a Pregl (*5*) tube, when either alkali (*2, 6*) or bromine water (*4*) was used as the absorbent. However, when samples of sulfanilamide were burned either by the above method or in the Grote apparatus (*6*), low results were obtained. The data for these determinations are shown in Table I. (Willits states that recently difficulties have been encountered in his laboratory with the catalytic method.) Samples of sulfanilamide were then burned by the Carius method, after which the resulting sulfate was titrated with barium chloride by the illuminated stand technique of Ogg, Willits, and Cooper. This procedure gave excellent results with sulfanilamide, sodium sulfite, and sulfanilic acid, and is now generally used in this laboratory. Table II gives the data for a number of analyses performed this way.

EXPERIMENTAL

Enough sample should be used so that 3 to 5 ml. of 0.01 N barium chloride will be needed for the titration. [Ogg, Willits, and Cooper (*4*) used 0.02 N barium chloride, while the authors obtained good results with 0.01 N. The barium chloride was standardized with 0.01 N potassium sulfate using the tetrahydroxyquinone indicator.] The sample is placed in a micro-Carius combustion tube along with 15 to 20 mg. of some pure sodium or potassium salt [such as oxalate, acid phthalate, chloride, etc. (*3*)] and 0.7 ml. of fuming nitric acid, specific gravity 1.49 to 1.50. The Carius tube is sealed and heated for about 7 or 8 hours at 250° C. After combustion, the tubes are opened, the mixture is quantitatively transferred to a small beaker, and the contents are evaporated to dryness on a steam bath. The residue of sodium or potassium acid sulfate is transferred to a cuvette (*4*), after which the solution is made alkaline with 0.1 N sodium hydroxide, using phenolphthalein as an indicator, and back-titrated with 0.01 N hydrochloric acid just to expel the color. From this point, the procedure is identical to that outlined by Ogg, Willits, and Cooper.

ACKNOWLEDGMENT

Table I. Determination of Sulfur in Compounds Using Catalytic Combustion and Ogg, Willits, and Cooper Titration

Compound	Empirical Formula	Weight of Sample, Mg.	0.01 N BaCl₂, Ml.	Percentage Sulfur Found	Percentage Sulfur Calculated
Sulfanilamide[a]	C₆H₈N₂O₂S	4.914	4.97	16.21	18.62
		5.049	5.35	16.99	
		4.331	4.53	16.77	
		4.539	4.59	16.21	
		5.021	4.87	15.55	
		4.430	4.88	17.66	
		3.989	4.20	16.88	
		4.472	4.70	16.84	
Sulfanilic acid	C₆H₇NO₃S.H₂O	4.509	4.75	16.89	16.77
		4.119	4.34	16.89	
		4.022	4.31	17.18	

[a] U.S.P. reference standard.

Table II. Determination of Sulfur in Compounds Using Carius Combustion and Ogg, Willits, and Cooper Titration

Compound	Empirical Formula	Weight of Sample, Mg.	0.01 N BaCl₂, Ml.	Percentage Sulfur Found	Percentage Sulfur Calculated
Sulfanilamide[a]	C₆H₈N₂O₂S	2.960	3.44	18.63	18.62
		3.480	4.11	18.93	
		3.230	3.77	18.71	
		3.280	3.87	18.91	
		5.345	6.22	18.66	
		2.488	2.88	18.56	
		2.822	3.29	18.69	
		2.489	2.89	18.61	
Sodium sulfite	Na₂SO₃	3.061	4.87	25.50	25.43
Sulfanilic acid	C₆H₇NO₃S.H₂O	1.716	1.80	16.81	16.77
Research[b]	C₁₀H₁₇O₆N₂SNa	5.228	3.29	10.09	10.14
	C₁₂H₁₁O₇N₂SNa	5.236	2.91	8.91	9.00
		4.845	2.76	9.13	
	C₈H₁₀O₂N₂S	4.364	4.26	15.65	16.17
		4.576	4.48	15.69	
	C₆H₈ON₂S	4.458	5.65	20.32	20.52
	C₂₅H₃₂O₆N₂S.¹/₂H₂O	7.778	2.96	6.10	6.44
	C₁₂H₁₇O₇N₂SNa	5.803	3.35	9.25	9.00

[a] U.S.P. reference standard.
[b] Purity of research compounds verified by analysis of other elements present.

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(6) Sundberg, O. E., and Royer, G. L., IND. ENG. CHEM., ANAL. ED., 18, 719 (1946).

Identification of Pennsylvania Lubricating Oils—Correction

In the article on "Identification of Pennsylvania Lubricating Oils" [Hersh, Fenske, Matson, Koch, Booser, and Braun, ANAL. CHEM., 20, 434 (1948)] a line was omitted from the text on page 443. The first sentence under the heading "Other Methods" should read: "In addition to the methods of identification described above, more elaborate procedures can be employed which utilize the physical and chemical characteristics of successive or selected fractions of the lubricating oil separated by distillation, solvent extraction, treatment with adsorbents, etc."

In line 4 of the next paragraph on page 443 "narrow-out fractions" should read "narrow-cut fractions." On page 438 under the subhead "Treatment with Adsorbents," line 11 should read: "1.9-cm. (0.75-inch) diameter."

Action of Nessler's Reagent on Amines

HERMAN A. LIEBHAFSKY AND LESTER B. BRONK

General Electric Company, Schenectady, N. Y.

THE authors were recently surprised to discover that Nessler's reagent on standing gives a more intense color with α-phenylnaphthylamine than with an equivalent amount of ammonia, a fact apparently not predictable from the extensive and complex literature on this reagent. The results of several exploratory experiments on this and other amines are accordingly given below.

PROCEDURE

An amount of ammonium chloride or of amine roughly equivalent to 7 micrograms of combined nitrogen was used in all determinations. Known solutions in water or in 95% ethyl alcohol when necessary (aniline, α-phenylnaphthylamine, diphenylamine) were prepared from the laboratory stock except in the case of α-phenylnaphthylamine, which was recrystallized once from alcohol and twice from petroleum ether. Appropriate volumes of these solutions were diluted with 25 ml. of water, whereupon 1 ml. of prepared Nessler's reagent was added, and the volume adjusted to 27 ml. with water. Transmittance measurements were then made on a recording spectrophotometer on about 2 ml. of the resulting solution or suspension; the cell thus contained about 0.5 microgram of combined nitrogen. Except when centrifuging was resorted to, any solid that had settled was redispersed by shaking

before the transmittance was measured. The pH of the final solutions was near 12.1.

Figure 1 contains results for ammonium chloride and for α-phenylnaphthylamine. The color of the ammonia compound developed rapidly, and no trace of solid matter was ever observed in this case. With the amine, the color appeared much more slowly, but eventually became much more intense. Scattering of light by suspended matter is responsible for much of the decrease in transmittance at the longer wave lengths (Figure 1, experiment 9); this decrease virtually disappeared when the suspensions were centrifuged (Figure 1, experiments 7 and 8).

Figure 2 gives results for several other amines. It is clear that diphenylamine resembles α-phenylnaphthylamine in its reaction with Nessler's reagent. If this reagent acts on the other amines at all, then—so far as the spectrophotometer can show—it does so to a smaller extent than on ammonia.

DISCUSSION

Nichols and Willits (1) concluded after a thorough investigation that the action of Nessler's reagent on ammonia produces in colloidal suspension a very insoluble compound of empirical formula $NH_2Hg_2I_3$. The results reported here for the two secondary aromatic amines seem to be in complete accord with this conclusion. In the first place, these amines have only one hydrogen on the
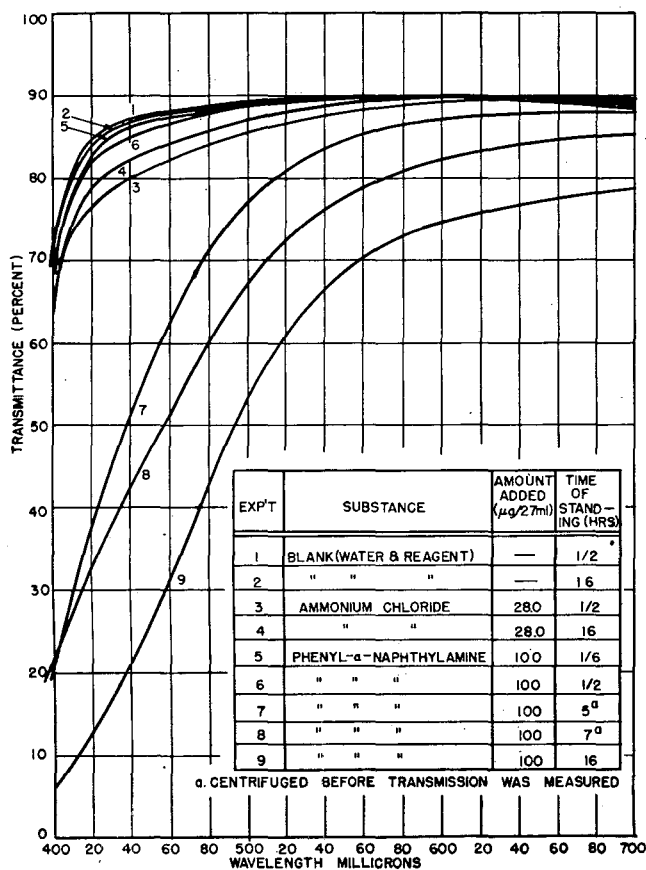

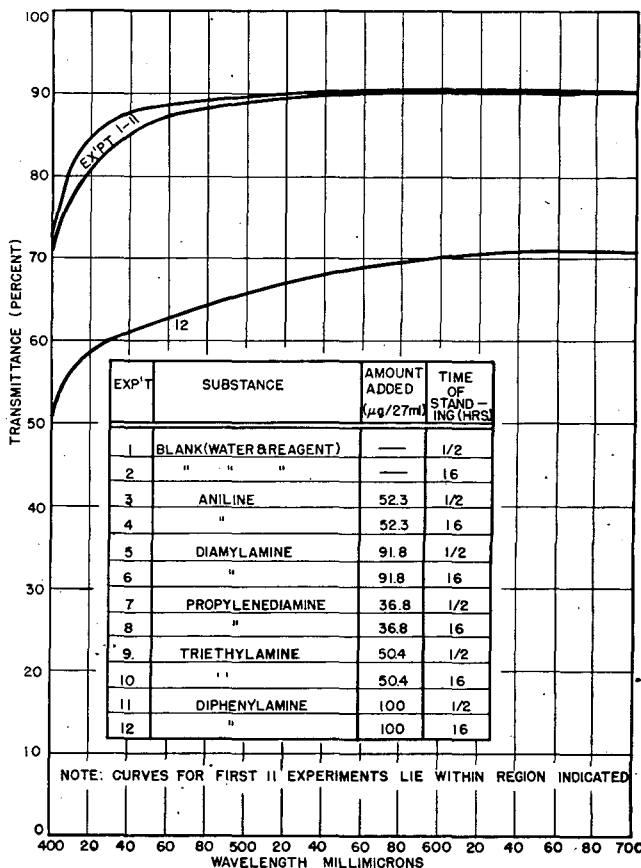Figure 1. Transmittance Measurements on Ammonium Chloride and α-Phenylnaphthylamine Combined with Nessler's Reagent

EXP'T	SUBSTANCE	AMOUNT ADDED (μg/27ml)	TIME OF STANDING (HRS)
1	BLANK (WATER & REAGENT)	—	1/2
2	" " "	—	16
3	AMMONIUM CHLORIDE	28.0	1/2
4	" "	28.0	16
5	PHENYL-α-NAPHTHYLAMINE	10.0	1/6
6	" " "	100	1/2
7	" " "	100	5a
8	" " "	100	7a
9	" " "	100	16

a. CENTRIFUGED BEFORE TRANSMISSION WAS MEASURED

Figure 2. Transmittance Measurements on Amines Combined with Nessler's Reagent

EXP'T	SUBSTANCE	AMOUNT ADDED (μg/27ml)	TIME OF STANDING (HRS)
1	BLANK (WATER & REAGENT)	—	1/2
2	" " "	—	16
3	ANILINE	52.3	1/2
4	"	52.3	16
5	DIAMYLAMINE	91.8	1/2
6	"	91.8	16
7	PROPYLENEDIAMINE	36.8	1/2
8	"	36.8	16
9	TRIETHYLAMINE	50.4	1/2
10	" "	50.4	16
11	DIPHENYLAMINE	100	1/2
12	"	100	16

NOTE: CURVES FOR FIRST 11 EXPERIMENTS LIE WITHIN REGION INDICATED

nitrogen atom, so that they could form compounds of the type $NH_2Hg_2I_3$, but not of some of the more speculative types that have been suggested as the nesslerization products of ammonia. In the second place, the aromatic radicals in these two amines should tend to make their nesslerization products insoluble in water.

The interaction of amines with Nessler's reagent obviously affords material for several interesting investigations.

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RECEIVED October 3, 1947.

Apparatus for Absorption of Carbon Dioxide in Mass Spectrometric Determination of the Carbon Isotopes

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AND
K. J. NEUVONEN, *Institute of Geology, University of Helsinki, Finland*

IN 1946 the authors carried out a series of combustions of carbonaceous materials from the Pre-Cambrian rocks of East Fennoscandia with the ultimate aim of obtaining material for mass spectrometric determination of the abundance ratio, C^{12}/C^{13}, of the carbon isotopes, the results of which work will be published elsewhere. One of the central problems of the investigation consisted of the development of a suitable combustion method and apparatus for converting the carbon into barium carbonate without the addition of carbon compounds from extraneous sources during the stages of the work. An apparatus was finally constructed for the purpose, and a short description of it is given below.

APPARATUS

A cylinder containing oxygen was connected with a pressure regulator to maintain a constant delivery pressure. The oxygen was washed with 40% sodium hydroxide solution in a gas-washing bottle, and allowed to pass another pressure regulator and a bubble counter. After passing a U-shaped absorption tube filled with calcium chloride and Ascarite, the gas entered a semimicro combustion tube placed in a combustion furnace. The latter half of the combustion tube was filled with cupric oxide.

The whole apparatus centers around the absorption assembly, which is presented in Figure 1.

An absorption bulb with side tubes for its connection with the combustion tube and with a small straight drying tube is filled with calcium chloride and Ascarite. To the upper end is sealed a fritted funnel of fine porosity (3G4, Schott & Genossen) and of 30-ml. capacity, and the lower end is provided, through a ground-glass joint, with a fritted micro filtering tube (12G3) of 2-ml. capacity and of medium porosity. The filtering tube is connected with a filter pump through a rubber stopper and a filtering flask.

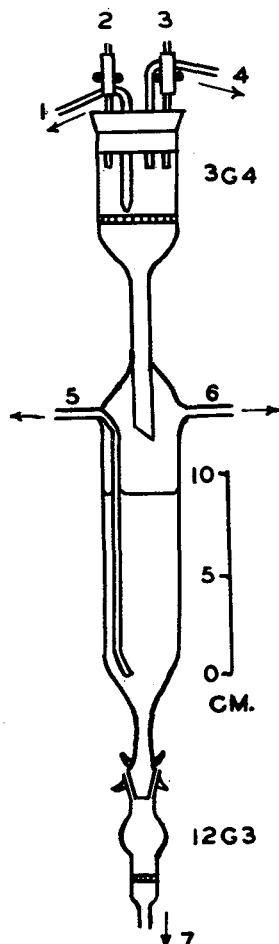The upper funnel is equipped with a rubber stopper and con-

Figure 1. Absorption Assembly

nected through it with two flasks, one of which contains saturated barium hydroxide solution and the other pure distilled water, such as that used for conductivity measurements. The flasks have air inlet tubes sealed with small calcium chloride–Ascarite drying tubes. The flow of water and barium hydroxide solution is regulated by means of pinchcocks attached to rubber tubing.

The rubber stopper is provided with glass and rubber tubings connected with a rubber bulb (atomizer). The rubber tubing has an interlying T-shaped glass tube to connect it with the filter pump. A small calcium chloride–Ascarite drying tube is also attached. A fourth piece of glass tubing, starting just above the fritted disk, serves as an exhaust for the funnel washings. Toward its lower end the tube is provided with a pinchcock.

PROCEDURE

Prior to the combustion, all air is expelled from the system by passing a current of oxygen through it for half an hour at a speed of 50 ml. per minute. The speed is then increased to 80 ml. per minute and part of the oxygen is drawn through the lower fritted funnel by connecting the latter with vacuum (15 minutes). For the next 20 minutes another part of the oxygen is forced through the upper fritted funnel by connecting the T-tube above the atomizer with vacuum. The flow is then adjusted to 20 ml. per minute, 100 ml. of barium hydroxide solution are pumped through the upper funnel into the absorption bulb, and the flow is regulated to 10 ml. per minute.

The charge in a platinum boat is heated cautiously over a small flame of a Bunsen burner and the combustion is allowed to proceed until about one half of the sample has been consumed, after which the flame is removed. The filter pump is started, the upper filter funnel is washed with a few milliliters of water, and 20 ml. of water are pumped into the absorption bulb. The flow of oxygen is adjusted to 5 ml. per minute, and the precipitated barium carbonate is filtered through the fritted filtering tube in 3 to 20 hours, depending on amount of the precipitate.

Next, 120 ml. of water are pumped into the absorption bulb and passed through the lower funnel, connected with vacuum. The filtration will take from 5 to 25 hours. The precipitate is washed with a few drops of water and the combustion continues to completion. The flow of oxygen through the drying tube attached to the side tube of the absorption jar is cut off, and the carbon dioxide–bearing oxygen is allowed to pass through the barium carbonate precipitate for 20 minutes. This is done in order to convert the barium hydroxide present in the precipitate into barium carbonate. The gas mixture is then allowed to pass through the upper fritted funnel for a few minutes, the precipitated barium carbonate is washed six or eight times with 2 to 3 ml. of water, and the oxygen–carbon dioxide mixture is once more allowed to pass through the precipitate. In 30 minutes the precipitate will become dry, and is placed in a drying cabinet and dried at 200° C. for 2 hours. Finally, the precipitate is transferred into a small glass tube which is heated for a moment over an asbestos board at approximately 600° C. and sealed.

During the combustion procedure the usual precaution of glass against glass in all joints was strictly observed. A series of preliminary combustions was carried out to ensure correct practice in all details. Blanks run with the apparatus failed to produce any barium carbonate precipitate, and it was concluded that the oxygen used in the combustion was of sufficient purity.

By means of this apparatus the authors carried out combustions of a series of graphites described above. In many cases this

mineral was extracted from the powdered rock samples by flotation or by treatment with hydrofluoric acid. The amount of graphite used for combustion was usually approximately 200 mg. and the recovered barium carbonate amounted to 50 to 300 mg., or enough for the subsequent determination of the carbon isotopes. The barium carbonate precipitates obtained were free from contamination by extraneous carbon compounds.

Microdetermination of *O*-Acetyl Groups

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IT OFTEN becomes necessary in structural investigations to determine accurately the number of *O*-acetyl groups, as distinguished from *N*-acetyl groups, in a compound containing both. The excellent method of Kunz and Hudson (7), as modified by Wolfrom, Konigsberg, and Stoltzberg (10), accomplished this objective and is now widely used for this purpose in sugar chemistry. It is based on the fact that *O*-acetyl groups are quantitatively liberated by 0.1 *N* sodium hydroxide in acetone solution, within a few hours at 0° C., while *N*-acetyl groups are not attacked under these conditions. However, the method in its present form requires about 100 mg. of substance, an amount which cannot always be spared in investigations on rare sugars. In connection with studies conducted in this laboratory on degradation products of streptomycin, it became desirable to adapt the procedure of Kunz and Hudson to a micro scale. Because the use of more dilute alkali was imperative in such a micro-modification, the completeness of saponification of mannitol hexaacetate by 0.01 *N* alkali at 0° and at room temperature (24° to 27° C.) was first investigated. The results summarized in Table I indicate that satisfactory values could be obtained after 2 hours at room temperature and that no untoward results are produced by increasing the reaction time.

Table I. Determination of *O*-Acetyl on Mannitol Hexaacetate

Temperature, °C.	Time, Hours	% Theoretical
0	2	60
	5	67
Room temp. (24–27°)	1	80
	2	99–100
	5	99–100

PROCEDURE

The sample (4 to 10 mg.) is weighed into a 50-ml. glass-stoppered flask and 5 ml. of C.P. acetone and 10 ml. of aqueous 0.01 *N* sodium hydroxide are added. The flask is immediately stoppered and set aside for 2 hours. At the end of this time 1 to 2 drops of phenol red are added and the solution is back-titrated with 0.01 *N* acid to a distinct yellow end point which will persist for at least 2 minutes. A blank determination on the acetone from time to time should not exceed 0.2 to 0.3 ml. of 0.01 *N* sodium hydroxide.

If the substance is precipitated by the standard solution, as happens occasionally, it is brought into solution again by the addition of another 5 ml. of acetone. When 10 ml. of acetone must be used, the blank correction is only slightly higher.

Certain water-insoluble compounds, such as sterol acetates, as well as deeply colored substances, cannot be conveniently analyzed by this method. Care must also be exercised in the interpretation of results when the substance being analyzed contains titratable basic or acidic groups, either in the free state or in a linkage from which they might be liberated by alkali under the above conditions.

The results in Table II show that the presence of *N*-acetyl

groups, in accordance with the findings of Wolfrom *et al.* (10), does not interfere.

Table II. Typical Analyses

Compound	*O*-Acetyl Found	*O*-Acetyl Calcd.
Acetanilide	0.0	0.0
Mannitol hexaacetate	59.2	59.5
	59.5	
	59.3	
	59.2	
β-Fructose pentaacetate	55.5	55.1
	55.3	
β-Glucose pentaacetate	54.8	55.1
	55.0	
Streptamine hexaacetate (8)	39.2	40.0
	39.0	
α-Hexaacetyldihydrostreptobiosamine (9)	36.5	36.4
β-Hexaacetyldihydrostreptobiosamine (9)	35.9	36.4
α-Pentaacetyldihydrostreptobiosamine (9)	31.2	31.3
	31.8	
α-Ethyl tetraacetylthiostreptobiosaminide diethyl mercaptal (5)	20.3	19.7
	20.4	
β-Ethyl tetraacetylthiostreptobiosaminide diethyl mercaptal (4)	20.4	19.7
α-Methyl pentaacetyldihydrostreptobios-aminide (3)	30.4	30.6
α-Methyl tetraacetylstreptobiosaminide dimethyl acetal (1)	21.6	22.8
	21.9	
α-D-Glucosamine pentaacetate	46.2	45.9
β-D-Glucosamine pentaacetate	46.0	45.9
α-*N*-methyl-L-glucosamine pentaacetate (6)	46.9ᵃ	42.7
	45.9	
β-Methyl tetraacetyl-D-mannopyranoside (2)	48.3	47.5
α-Methyl tetraacetyl-D-mannopyranoside (2)	47.7	47.5
α-Thioethyl tetraacetyl-D-mannoside (2)	44.2	43.8
β-Thioethyl tetraacetyl-D-mannoside (2)	43.4	43.8

ᵃ Results on this compound as well as other *O*- and *N*-acetylated derivatives of *N*-methylglucosamine investigated after this paper had been submitted, were consistently high. The cause of the apparent instability of the *N*-acetyl group under these conditions is being investigated.

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RECEIVED September 23, 1947.

Photoelectric Determination of the Color of Corn Sirup

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MEASUREMENT of the color of corn sirup presents certain difficulties not ordinarily encountered with other materials. The paleness of the colors involved necessitates the use of a long column of sample; the extremely high viscosity of the sirup necessitates the use of a sample container which can be filled and cleaned easily. For routine daily color measurements many sample tubes are required; a clean dry tube is needed for each sample, as the tubes cannot be emptied and rinsed with a portion of the next sample. In this laboratory approximately 35 color measurements are made each day, and it is important that the sample tubes be inexpensive.

Cylindrical tubes of Kimble glass (1.25 inches in outer diameter, 5 inches long, open at one end, and having a molded flat bottom) have been used satisfactorily in a Lumetron Model 402E photoelectric colorimeter. For this purpose the instrument is set up so that it stands on what would normally be the right end. In this position of the instrument the sample compartment is vertical and can accommodate the 5-inch tube. (The Photovolt Corp. now manufactures Lumetron Model 450 to accommodate vertical tubes. This instrument has lower sensitivity than Model 402E but would probably give satisfactory results.) The photocell at the bottom of the compartment is protected by a glass sheet $1/32$ inch thick; tubes are centered in a holder consisting of a fiberboard slab 0.125 inch thick with a 1.25-inch hole cut in it. The holder is wedged into the compartment just above the glass sheet. Transmittance values are read in the normal way.

COLOR OF CORN SIRUP

A typical light absorption curve for corn sirup is given in Figure 1 (curve obtained with the Coleman Universal spectrophotometer); maximum absorption is at 380 mμ. In adapting the Lumetron instrument to the present use, it was found that a 420 mμ filter (consisting of a 6-mm. thickness of Corning No. 5113 blue glass) and a 4.75-inch column of sirup gave the most
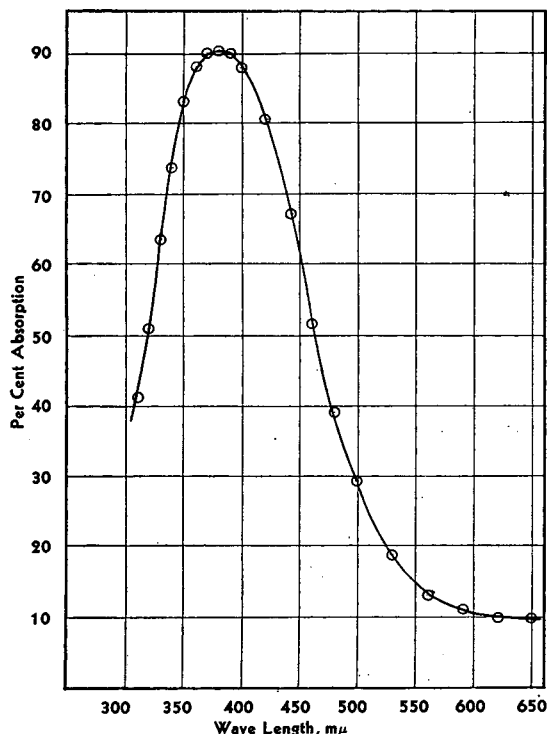

Figure 2. Curve Relating Transmittance and Color of Corn Sirup
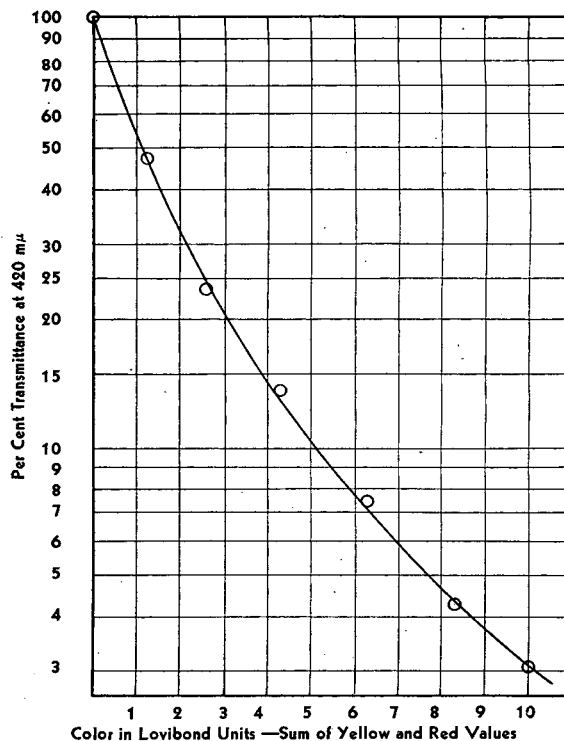

Figure 1. Absorption Curve for Corn Sirup

convenient spread of readings on the transmittance scale. A 380 mμ filter increased the sensitivity of the measurements, but crowded the readings into the lower portion of the scale.

It was desired to retain both the standard sample length of about 5 inches and the Lovibond color standards previously in use in the industry. A series of samples of corn sirup of various colors was therefore matched visually against Lovibond slides (series 510 yellow, series 200 red) in a split-field comparator, then read in the Lumetron. Results are plotted in Figure 2. Although the points do not fall on a straight line, this may indicate merely that the Lovibond units are not proportional to density. The curve is a convenient means of translating transmittance readings into Lovibond values. Results are reported in Lovibond units.

DISCUSSION

The method is rapid. Results are adequately accurate for refinery control if precautions are observed.

All sample tubes should be cleaned carefully and checked against a standard tube before being put into service. The standard tube is arbitrarily set at 100% transmittance when filled with distilled water, and only those tubes showing between 98 and 102% transmittance should be used. Tubes with more nearly flat bottoms are available, but are considerably more expensive. They should be used when exact measurements are required.

The sample should be poured very carefully into the tube to prevent trapping air bubbles in the sirup, as these lead to falsely low transmittance readings. If any bubbles are present the tube should be allowed to stand in a warm place until the bubbles come to the top and can be scraped off with a spatula. The level of corn sirup in the tube should be adjusted, if necessary,

so that the sirup is just 0.25 inch from the top. This will prevent any lens effect of the meniscus from interfering with the reading. After the level has been adjusted, the tube should be checked visually to make sure that the surface is flat. This can be done by looking down through the full length of the sample at the bottom of the tube, which should appear as a smaller circle inside the mouth of the tube. If the bottom cannot be seen through

the mouth of the tube or is distorted, the surface is not flat and must be scraped.

The glass sheet protecting the photocell must be cleaned carefully and the bottoms of the sample tubes must be kept clean to prevent partial blocking of the photocell.

This method has been used daily for the past two years with excellent results on sirups in the Baumé range 20 to 44.

BOOK REVIEWS

A Text-book of Practical Organic Chemistry Including Qualitative Organic Analysis. *Arthur I. Vogel.* xxiii + 1012 pages. Longmans, Green and Co., 55 Fifth Ave., New York 3, N. Y., 1948. Price $10.50.

A few remarks taken from the Preface will reveal the purpose and general contents. "Many of the new procedures and much of the specialized technique developed and employed in (the author's) researches are incorporated. . . . .It is not expected that the student will employ even the major proportion of the operations described, but a knowledge of their existence is thought desirable for the advanced student. . . . . A short theoretical introduction precedes the detailed preparations. . . . .The textbook is intended to meet the requirements of the student throughout the whole of his training. . . .. It will also provide an introduction to research methods in organic chemistry and, it is hoped, may serve as an intermediate reference book for practising chemists."

Here, with the notable exception of quantitative organic analysis, is a one-package presentation of laboratory work in organic chemistry on all levels. As a teaching instrument, however, it may not find wide use in our American schools, for it embraces much more material than can be presented in any ordinary laboratory course.

Chapters I and II (230 pages) cover the "Theory of General Technique" and "Experimental Technique." Preparations are treated begin on page 231 (Chapter II) and conclude on page 887 (end of Chapter X). Qualitative organic analysis merits only 66 pages (Chapter XI), although the previous chapters feature tables of physical properties and assorted diagnostic reactions useful for identification. The Appendix, entitled "Literature of Organic Chemistry," includes information on preparation of palladium catalysts, periodic acid in qualitative organic analysis, etc. The index is ample.

The preparations are very numerous and appear to be well chosen. In nearly every instance the detailed example is followed by a number of "cognate preparations." Thus the directions for making *n*-butyl iodide by the phosphorus-iodine method are followed by brief instructions for making thirteen other iodides in the same general way. In a few instances the recommended procedure is not the best available. For example, the preparation of dimethylethynylcarbinol (p. 454) employs the sodamide method rather than the sodium acetylide which gives better yields, is much less hazardous, and can be adapted to a larger scale.

The paper is of good quality, the printing is excellent, and there are remarkably few typographical errors. A regrettable feature is that citations to the original literature are not given, although there are numerous references to firms supplying special apparatus and chemicals.

Vogel's textbook will prove a rich source of information for graduate students and other bench workers in organic chemistry. It should be available in every library that claims to serve their needs.

G. F. HENNION

Cyanogen Compounds, Their Chemistry, Detection, and Estimation. *H. E. Williams.* 2nd ed. xvi + 443 pages. Longmans, Green and Co., 55 Fifth Ave., New York 3, N. Y., 1948. Price, $10.50.

Since 1915 those engaged in the field of cyanogen compounds have turned to Williams when confronted with a problem. For some years the book was inadequate, but now the second edition has appeared in modified and greatly expanded form. The new edition has omitted

methods of manufacture, which could not be adequately treated in one volume and still do justice to the other material covered.

Considerable, although by no means complete information is given on such compounds as cyanamide, dicyandiamide, guanidines, and melamine, which even 10 years ago were practically rare chemicals but are now produced in considerable quantity.

As in the first edition the chemistry of the cyanides, cyanates, thiocyanates, and their complexes has been treated extensively and brought up to date. This portion of the book is outstanding and references to the scientific literature are extensive and complete.

The analytical section has been expanded to include the newer organic compounds. The author points out in the introduction that "several of the methods when used for the first time require manipulatory practice, however skilled the hands." This is especially true of the newer organic compounds.

No one active in the field of cyanogen compounds can afford to be without the book. L. J. CHRISTMANN

Proceedings of the Society for Experimental Stress Analysis. Edited by *C. Lipson* and *W. M. Murray.* Vol. V, No. 2. Addison-Wesley Press, Inc., Cambridge 42, Mass. Price $6.

Methods in Medical Research

"Methods in Medical Research," a series of annual volumes devoted to methods and techniques, is to be published by the Year Book Publishers, Inc., Chicago, Ill. The Governing Board is composed of Irvine H. Page, A. C. Ivy, Colin M. MacLeod, Carl F. Schmidt, Eugene A. Stead, and David L. Thomson. Volume I, under the editorship of Van R. Potter, University of Wisconsin, was available in May 1948, and succeeding books are due every January. Contents of Volume I include: "Assay of Antibiotics," by Henry Welch; "Circulation," by Harold D. Green; "Selected Methods in Gastroenterologic Research," by A. C. Ivy; and "Cellular Respiration," by Van R. Potter.

Correspondence

Constant Level Control for Water Baths

SIR:

The type of apparatus discussed by Snell (2), was described by the writer in March 1942 (1). Although I used this apparatus in 1938, it is so simple and straightforward that I would be surprised to find that I was the first to utilize it. This communication is not to claim priority but to point out two details that may be of interest.

As will be seen from Figure 2 (1) reproduced here, the simple siphon shown in Snell's diagram is slightly modified (see B). Owing to the vacuum created at the top of the siphon, air bubbles tend to form there and break the siphon action. I, therefore, included an air trap in the form of an inverted funnel with two inlets at the bottom and an outlet at the top, the latter closed by a rubber tube and a clip. By
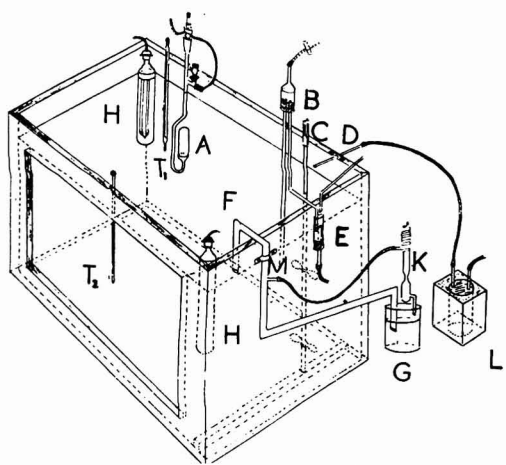
Figure 2 (1)

this means the apparatus was found to function without a break for several months at a time; by applying suction to the rubber tube the siphon can also be easily started without dismantling the unit.

The second item of interest is the siphon system, *FMKG*. It was necessary in the water bath concerned to add cold water continuously to the bath (for the purpose of maintaining constant temperatures below room temperature). In avoiding flooding, this second siphon system was effective and worked without attention for several years. It consists of large-diameter pipe, *FM* (1-inch iron pipe was used), one limb of which dips into the bath at the level to be controlled and the second into the water seal, *G*. Water vacuum pump *K* ran continuously and thus each time the level in the bath rose to a predetermined point the siphon would automatically start and empty the excess water. The function of the pump was simply to start the siphon; its capacity was too small for maintaining a constant level. Only two points have to be remembered in utilizing this system: The capacity of the siphon tube should be larger than the input of the water into the bath, and the difference in height between the constant level and the top of the siphon should be smaller than the difference in height between *M* and the level in the liquid seal, *G*.

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Northfleet, Gravesend,
Kent, England

CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology
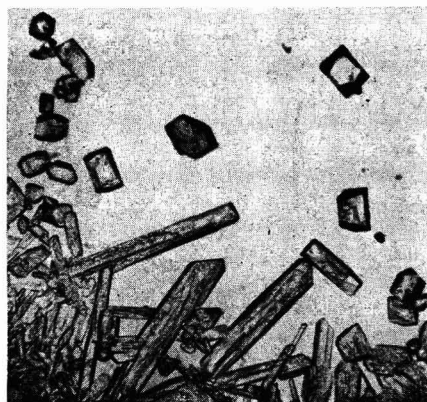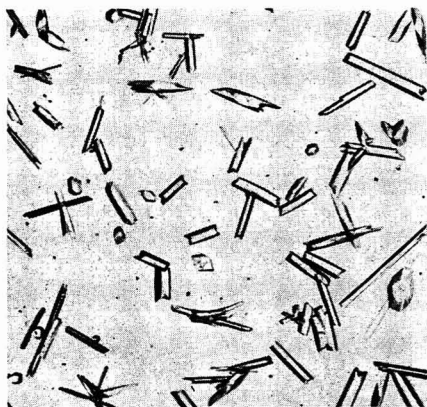

Figure 1 (lower). Crystals of *p*-Methyl Aminophenol Sulfate from Water on Microscope Slide. Figure 2 (upper). Crystals of *p*-Aminoazobenzene from Thymol on Microscope Slide
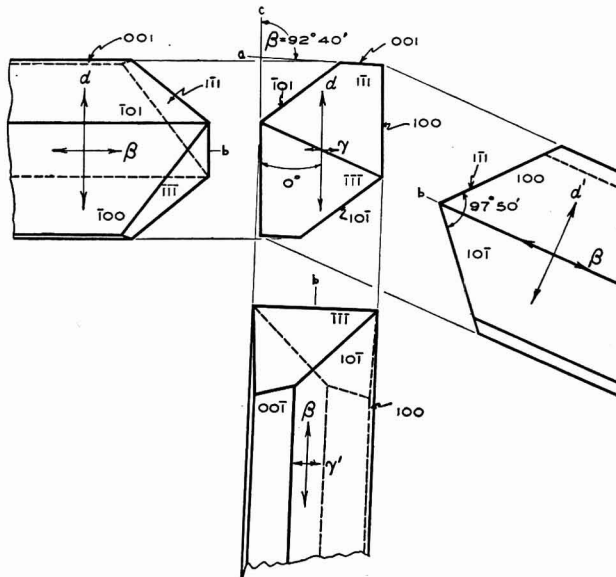

Figure 3. Orthographic Projections of Typical Crystal of *p*-Methyl Aminophenol Sulfate

6. *p*-Methyl Aminophenol Sulfate (Metol, Elon)

Crystals of *p*-methyl aminophenol sulfate suitable for microscopic investigation can be obtained from aqueous solution on a microscope slide. Crystals for x-ray diffraction and goniometry can be prepared by slow cooling of aqueous solutions.

CRYSTAL MORPHOLOGY (determined and checked by W. C. McCrone and J. W. Cook).

Crystal System.   Monoclinic.

Form and Habit.   Elongated parallel to *b* with the forms: orthopinacoid {100}; basal pinacoid {001}; positive hemiorthodome {101}; and negative hemibipyramid (111), ($\bar{1}1\bar{1}$), ($\bar{1}1\bar{1}$), and (1$\bar{1}$1).

Axial Ratio. $a:b:c$ = 3.180:1:2.512 (goniometry).

Interfacial Angles (Polar).   001$\wedge$100 = 87° 20'; 100$\wedge$10$\bar{1}$ = 53° 20'; $\bar{1}$01$\wedge$001 = 39° 20'; 111$\wedge\bar{1}1\bar{1}$ = 82° 10'.

Beta Angle.   92° 40' (goniometry); 93° 30' (x-ray).

X-RAY DIFFRACTION DATA (determined and checked by J. F. Whitney, I. Corvin, and M. Tull).

Cell Dimensions.   *a* = 18.61₅ Å.; *b* = 5.82₆ Å.; *c* = 14.60 Å.

Formula Weights per Cell.   4.

Formula Weight.   344.38.

Density.   1.416 (buoyancy); 1.434 (x-ray).

Principal Lines

Index	d	I/I_1
200	9.33	0.15
002	7.37	0.53
$\bar{3}$01,010	5.87	0.40
110	5.60	0.14
011	5.44	0.16
400	4.66	1.00
112	4.43	0.17
311,$\bar{4}$02	3.99	0.17
500,013	3.66	1.00
004,$\bar{3}$03	3.76	0.24
$\bar{2}$04	3.48	0.54
...	3.37	0.19
600	3.09	0.09
020,005	2.92	0.093
220	2.81	0.143
221	2.74	0.029
$\bar{2}$06,603	2.67	0.029
$\bar{2}$22,222	2.61	0.143
420	2.49	0.086
...	2.43	0.043
$\bar{5}$05,$\bar{4}$22	2.37	Weak
800	2.33	Weak
0$\bar{2}$4	2.28	Weak
$\bar{2}$24	2.25	Weak
505,224	2.20	Weak
620	2.13	Weak
900,$\bar{4}$24	2.08	Weak
424,622	2.03	Weak
030,130	1.95	Weak
026	1.88	Weak
033	1.84	Weak

OPTICAL PROPERTIES (determined by J. W. Cook and W. C. McCrone).

Refractive Indices (5893 Å.; 25° C.). α = 1.508 ± 0.001; β = 1.607 ± 0.001; γ = 1.694 ± 0.002.

Optic Axial Angles (5893 Å.; 25° C.). $2V$ = 81°; $2H$ = 89°. Dispersion. $r > v$.

Optic Axial Plane.   010.

Extinction. $\alpha \parallel$ 100.

Sign of Double Refraction.   Negative.

Molecular Refraction (R) (5893 Å.; 25° C.). $\sqrt[3]{\alpha\beta\gamma}$ = 1.602. R (obsd.) = 83.2. R (calcd.) = 90.1.   (R, sulfur, assumed = 8.00).

FUSION DATA (determined by W. C. McCrone).

p-Methyl aminophenol sulfate melts with decomposition at about 250° to 260° C.

7. *p*-Aminoazobenzene (Aniline Yellow S)

Good crystals of *p*-aminoazobenzene are difficult to prepare. Best results are obtained by recrystallizing from alcohol at room temperature or slightly above, by very slow dilution with water. Crystals suitable for x-ray diffraction or goniometry can be grown over a 2- to 3-hour period.   Well-formed crystals for microscopic examination may be obtained by slow cooling of a saturated thymol drop on a microscope slide.

p-Aminoazobenzene II crystallizes spontaneously from supercooled solutions and melts.   It is, however, very unstable and transforms readily to the stable form described below.   No effort was made to determine the properties of the unstable form beyond those reported under thermal data.

CRYSTAL MORPHOLOGY (determined and checked by W. C. McCrone).

Crystal System.   Monoclinic.

Form and Habit.   Elongated parallel to *c* with prisms {110}; orthopinacoid {100}; basal pinacoid {001}; hemiorthodome (101) and (10$\bar{1}$).
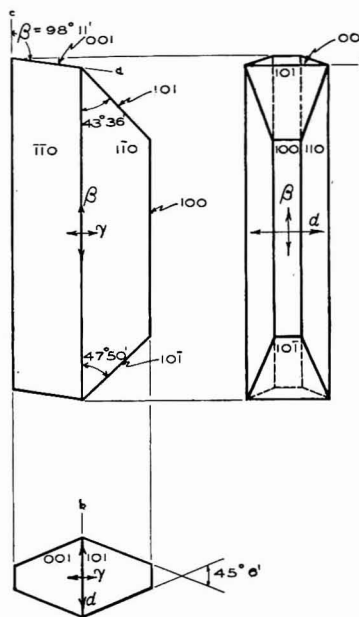

Figure 4.   Orthographic Projections of Typical Crystal of *p*-Aminoazobenzene

Axial Ratio. $a:b:c$ = 2.530:1:2.442 (x-ray).

Interfacial Angles.   101$\wedge$10$\bar{1}$ = 91° 26'; 101$\wedge$100 = 43° 36'; 10$\bar{1}$$\wedge$100 = 47° 50'; 10$\bar{1}$$\wedge$001 = 38° 13'; 10$\bar{1}$$\wedge$00$\bar{1}$ = 50° 21'.

Beta Angle.   98° 11' (x-ray).

X-RAY DIFFRACTION DATA (determined and checked by J. Whitney, I. Corvin, and M. Tull).

Space Group. $C^5_{2h} \rightarrow P2_1/n$ (1).

Cell Dimensions.   *a* = 13.69 Å.; *b* = 5.604 Å.; *c* = 14.18 Å. *a* = 13.69 Å.; *b* = 5.604 Å.; *c* = 14.18 Å. (1).

Formula Weights per Cell.   4; 4 (1).

Formula Weight.   197.11.

Density.   1.20; 1.174 (1).

Principal Lines

Index	d	I/I_1
200	9.05	0.05
200	6.86	0.13
202,011	5.25	1.00
111	4.97	0.38
$\bar{2}$02,300	4.56	0.97
112,210	4.31	1.00
...	4.17	0.04
$\bar{2}$11	4.02	0.64
004	3.55	0.77
402	3.28	0.38
$\bar{2}$04	2.93	0.38
020	2.79	0.09
022,220	2.60	0.05
222	2.48	0.09
...	2.44	Weak
$\bar{2}$22	2.39	Weak
206,$\bar{4}$04	2.31	Weak
024	2.19	Weak
$\bar{2}$06,422	2.12	Weak
$\bar{6}$02	2.07	Weak
007,$\bar{4}$22	2.01	Weak
700,$\bar{3}$06	1.96	Weak
...	1.87	Weak
606,226	1.79	Weak
008,620	1.76	Weak
330	1.73	Weak
...	1.63	Weak

OPTICAL PROPERTIES (determined by W. C. McCrone).

Refractive Indices (5893 Å.; 25° C.). α = 1.675 ± 0.003; β = 1.81 ± 0.01; γ = 2.02 ± 0.02.

Optic Axial Angles (5893 Å.; 25° C.). $2V = 85° \pm 2°$.
Dispersion. $r > v$.
Optic Axial Plane. $\perp$ 010 with $\beta \| c$.
Sign of Double Refraction. Positive.
Extinction. $\beta \| c$.
Pleochroism. X (light yellow); Y (dark yellow); Z (orange).
Molecular Refraction (R) (5893 Å.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.83$.
R (obsd.) = 71.9. R (calcd.) = 63.1.
FUSION DATA (determined by W. C. McCrone).

1. p-Aminoazobenzene melts at 125–126° C. with slight sublimation.

2. If melted completely the melt may supercool almost to room temperature; in this case an unstable polymorph crystallizes spontaneously. Almost instantly these crystals transform from many nuclei to the stable form. There is also evidence of boundary migration for the unstable form.

3. A meltback leaving some seed crystals always gives the stable form growing as broad rods usually showing a slightly off-center optic axis interference figure ($2V = 85°$; (+); $v > r$)

LITERATURE CITED

(1) Prasad, M., and Kapadia, M., *Indian J. Physics*, 8, 77–81 (1933).

THE ANALYST'S CALENDAR . . . . .

Nucleonics and Analytical Chemistry Symposium

FINAL PROGRAM

Northwestern University . . . . . Evanston, Ill . . . . . August 13 and 14, 1948.

THE final program of invited papers for the First Annual Summer Symposium on Analytical Chemistry has been completed and is presented below.

Clement J. Rodden, chief, Section of Uranium and Related Materials, National Bureau of Standards, and general chairman of the symposium, has selected a group of top-flight experts to cover the timely subject of the meeting—"Nucleonics and Analytical Chemistry."

This symposium will inaugurate a series of annual summer sessions to be sponsored by the Division of Analytical and Micro Chemistry and ANALYTICAL CHEMISTRY.

S. C. Lind, dean of the Institute of Technology of the University of Minnesota and editor of the *Journal of Physical and Colloid Chemistry*, is serving as honorary chairman, and Laurence D. Frizzell of Northwestern University is chairman of the committee on local arrangements.

In addition to the papers, plans are being made for both prepared and informal discussion. An especially valuable part of the meeting will be a demonstration by the Argonne National Laboratory of equipment and apparatus of special interest in the field of radiochemistry. Arrangements for this demonstration are being made by W. M. Manning, director of the division of chemistry of Argonne.

Another highlight of the meeting will be a dinner at the Edgewater Beach Hotel, at which it is expected a member of the United States Atomic Energy Commission, will give the principal address.

The Sherman Hotel has been designated as the Chicago headquarters. Its management has allocated a certain number of rooms. Requests for reservations should be addressed directly to the hotel at Randolph, Clark, and LaSalle Sts., Chicago, Ill. Specific mention should be made that you are attending the Symposium on Nucleonics and Analytical Chemistry of the AMERICAN CHEMICAL SOCIETY.

Although it is believed that a sufficient number of rooms will be available, anyone expecting to attend should get his reservation in as quickly as possible.

Friday, August 13, 1948

1—10:00. **Introductory Remarks.** C. J. RODDEN, National Bureau of Standards.

2—10:10. **Instruments Employed in the Measurements of Radioactivity.** C. J. BORKOWSKI, Oak Ridge National Laboratory.

3—11:15. **Techniques Employed in Applied Radiochemistry** W. H. SULLIVAN, Radiation Laboratory, San Francisco Naval Yard.
Methods for preparation of samples for counting purposes with consideration of coincidence losses, geometry, scattering, and self-absorption factors

12:20. Lunch, Evanston Restaurants.

4— 1:45. **Radioactive Isotopes as Tracers.** PETER YANKWICH, University of California.
The use of the property of radioactivity as a tag for the element possessing it. Thus, when an active isotope of an element is used in the presence of common inactive isotopes, it may serve to indicate the path of the stable isotopes throughout the various chemical or physical changes they may undergo.

5— 2:50. **Determination of Natural Occurring Radioactive Elements.** C. J. RODDEN, National Bureau of Standards.
Radiochemical and chemical methods for the determination of the radioactive elements occurring in nature—for example, radium, uranium, thorium, etc.

6— 3:30. **Demonstration by Argonne National Laboratory.** Introduction by W. M. MANNING.

7:30. Dinner, Edgewater Beach Hotel.

Saturday, August 14, 1948

7— 9:00. **Activity Analysis.** D. N. HUME, Massachusetts Institute of Technology.
The quantitative determination of the radioactivity due to a given element in a complex mixture of radioactive elements employing carrier techniques. For example, the analysis of the fission products of U^{235}.

8—10:05. **Activation Analysis.** G. E. BOYD, Oak Ridge National Laboratory.
The presence of certain elements in a sample can often be established, with or without the help of a chemical separation, by means of their characteristic half-lives, after the substance has been activated in some manner, as, for example, with neutrons, deuterons, protons, alpha-particles, etc.

11:30. Lunch.

9—12:45. **Industrial Applications.** J. W. IRVINE, JR., Massachusetts Institute of Technology.

10— 1:50. **Preparation and Procurement of Radioactive Materials.** N. H. WOODRUFF AND S. A. LOUGH, Isotope Division, U. S. Atomic Energy Commission.

Constant-Level Apparatus. Milton S. Schechter and H. L. Haller, U. S. Department of Agriculture, Bureau of Entomology and Plant Quarantine, Beltsville, Md.

A N apparatus for maintaining a constant level of liquid during distillation, evaporation, or filtration is of considerable utility in some laboratories. Two excellent designs have been described by Holmes [IND. ENG. CHEM., ANAL. ED., 12, 483 (1940)], and the apparatus illustrated is a modification of his column for distilling flask.
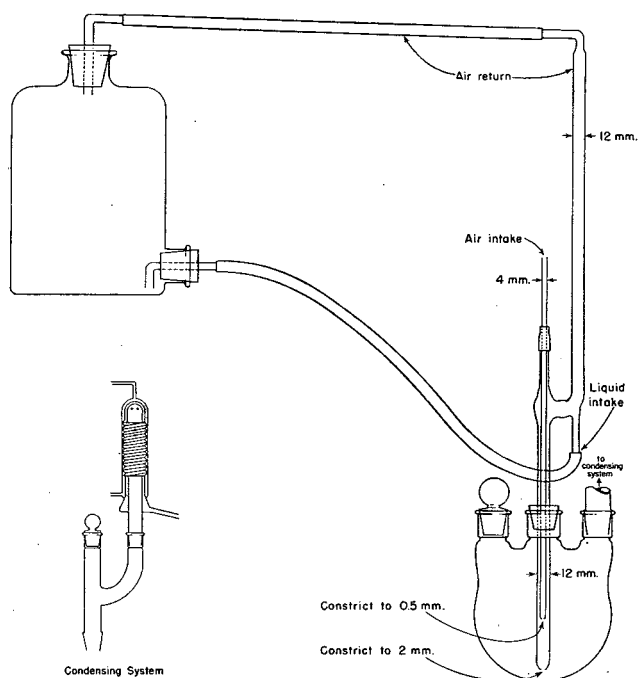

Figure 1. Diagram of Apparatus

The advantages of the new design are simplicity of fabrication, adaptability to flasks of different sizes, and ease of obtaining any desired level during the distillation. The last point is sometimes important in cases of bad foaming and in the distillation of thermolabile substances, where the level of liquid in the flask should be maintained above that of the liquid in the heating bath (oil, water, or steam). The apparatus is not suitable for distillations under reduced pressure.

Although a large bottle with the siphon arrangement illustrated by Holmes may be used, the gravity-feed reservoir bottle described herein has the advantage that the siphoning action cannot be broken by an accumulation of air bubbles in the feed line. The bottom of the bottle should be at a higher level than the liquid-intake arm of the constant-level apparatus.

It is desirable to have the upright glass-tubing section of the air return extend as high as the top of the reservoir bottle, so that the tubing will not be in constant contact with the solvent. The tubing should be supported without kinking or looping, to prevent trapping of liquid in it. The tubing from the reservoir bottle to the liquid intake should be of high quality and thick-walled. A special type of lined tubing is available commercially, which will withstand the prolonged action of halogenated solvents such as chloroform.

The apparatus seems to work more smoothly and with less turbulence of the liquid if the bottom of the air-intake tube is constricted to about 0.5 mm. in inside diameter. If the turbulence in the air-return tube is still so great that the solvent surges up the tube into the reservoir bottle, the rate of air intake should be adjusted by attaching a slightly opened glass stopcock or a piece of glass tubing drawn to a coarse capillary to the top of the air-intake tube by means of rubber tubing. The condensing system should be able to handle a rapid vapor flow, so that excessive back pressure will not build up in the distilling flask and cause difficulty in adjusting the level. In the absence of back pressure the liquid in the distilling flask will be at the same level as the bottom of the air-intake tube. The greater the back pressure, the greater the depression of the level of liquid. The level in the flask may be changed by sliding the air-intake tube up or down in the rubber sleeve.

Although the constant-level apparatus may be used with any distillation setup into which it can be inserted, the three-necked standard-joint flask and condensing system illustrated offer certain obvious advantages for use in the recovery of solvents. This equipment, with the rubber tubing wired in place, has been used with excellent results in the redistillation and recovery of large amounts of low-boiling solvents. The procedure described by Holmes for starting and operating the apparatus should be followed.

A Semimicro Distilling Head. Helmut M. Haendler, University of New Hampshire, Durham, N. H.

A DISTILLING head, with low holdup, was needed for fractionating small quantities of organic fluorine compounds. The semimicrohead described was adapted from several existing heads, most of which were suitable only for macro- or micro-distillations, and has been used satisfactorily on a 23-plate, helices-packed, 10-mm. diameter column. The condenser is attached directly to the head, and the thermometer is suspended so that the bulb reaches into the vapor zone of the head. The dimensions can be varied to suit the installation, but the vertical distances should be as short as possible.
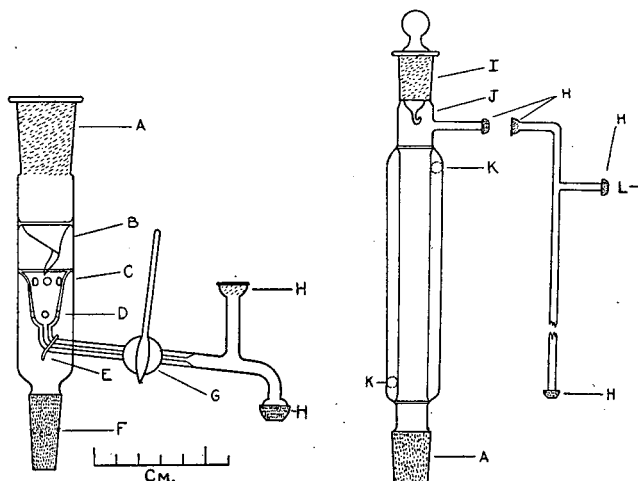
A, 29/42 standard taper joint
B, wide funnel with drip point
C, 4- to 5-mm. holes around circumference of inner cup
D, 4 drainage holes
E, ridge around tube with drip point

F, 14/35 standard taper joint
G, 1-mm. stopcock
H, 12/5 semiball joint
I, 24/40 standard-taper joint
J, thermometer hook
K, water inlet and outlet
L, to trap