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ANALYTICAL CHEMISTRY

Duplicate

DECEMBER 1947

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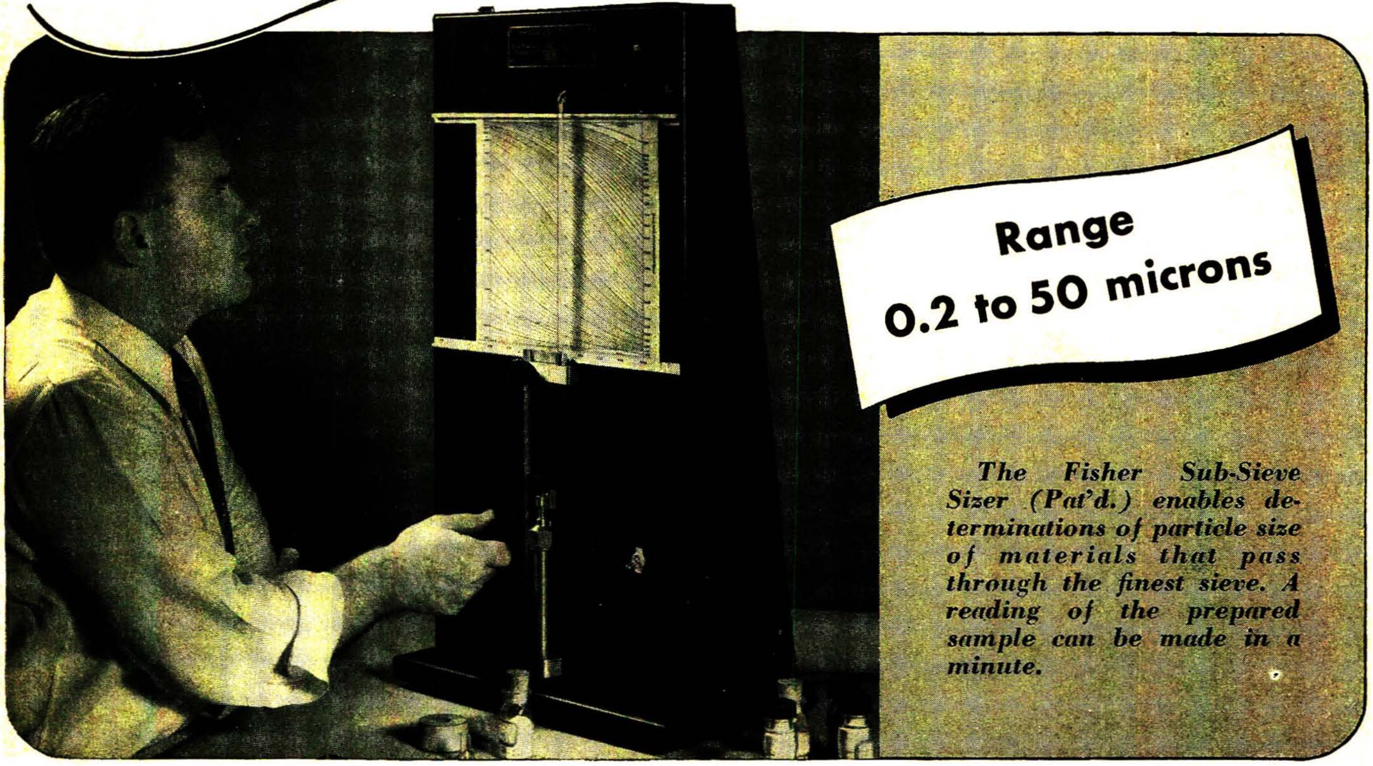

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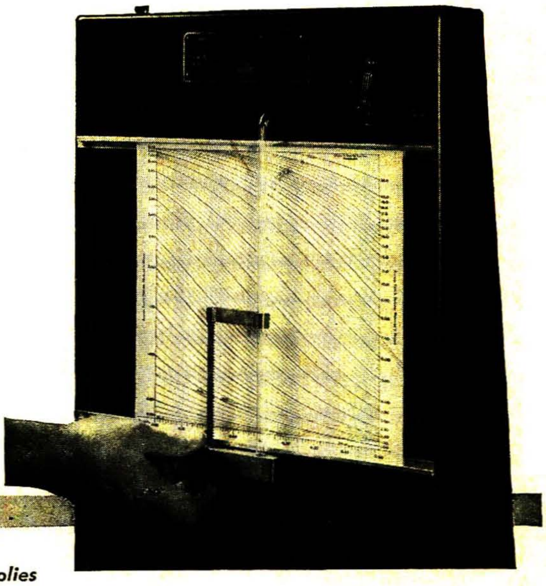

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INDUSTRIAL AND ENGINEERING CHEMISTRY *covering the field of . . .*

ANALYTICAL CHEMISTRY

Analytical Edition, Industrial and Engineering Chemistry **Volume 19 Number 12** **Consecutive Number 24**

Issued December 19, 1947

Symposium on Statistical Methods in Experimental and Industrial Chemistry

Discussion of Symposium Papers

Determination of Organic Peroxides

MICROCHEMISTRY

NOTES ON ANALYTICAL PROCEDURES

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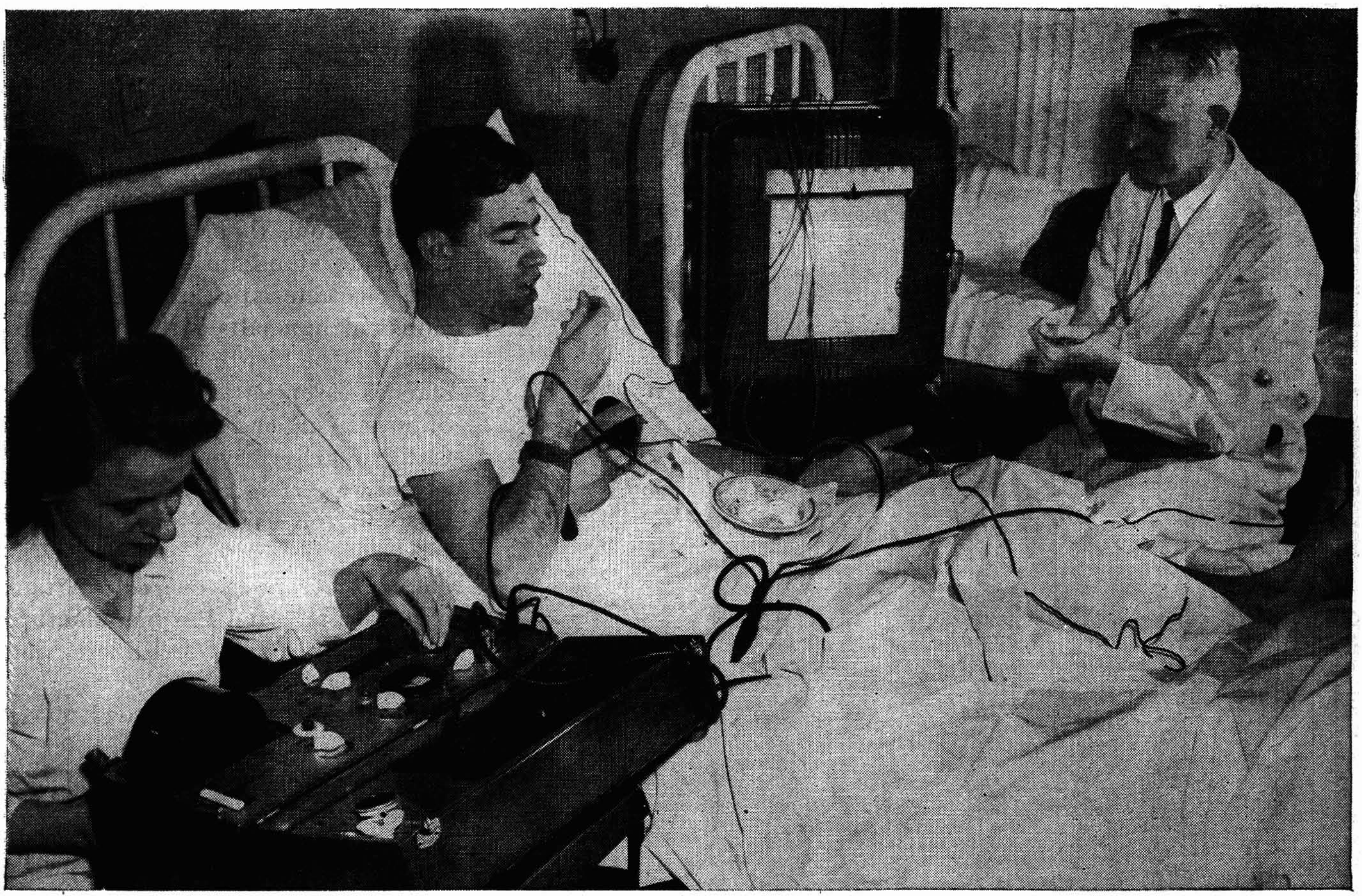

For testing the effect of food temperature on the flow of blood, Dr. Austin Henschel (right), Assoc. Prof. of Physiological Hygiene at Univ. of Minnesota, uses a Speedomax Recorder to check skin temperature of a student eating ice cream.

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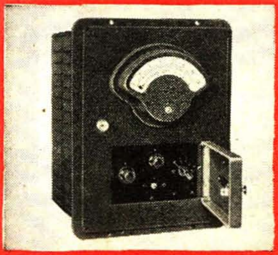

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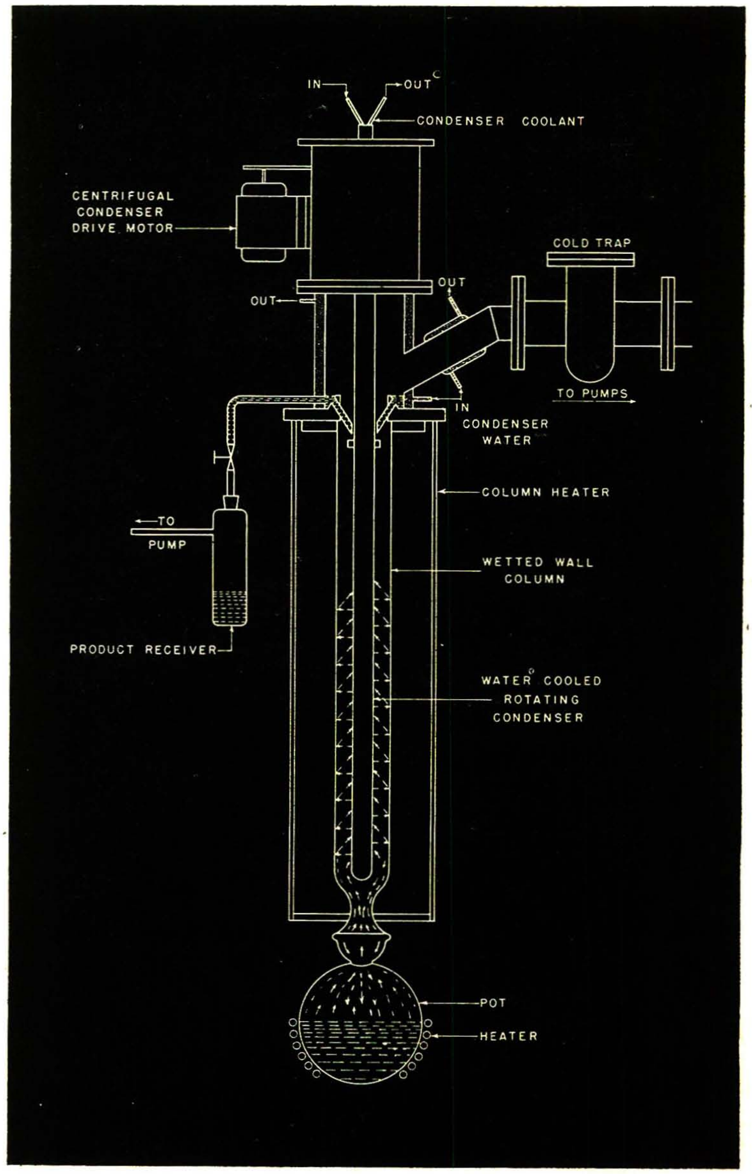

The unique principles of the centrifugal condenser type still are illustrated above. Rising vapor from the pot condenses on the cooled rotating cylinder. Condensate is then hurled off the condenser surface by centrifugal force and re-vaporized from the heated column. This cycle is repeated many times as the vapor moves up the annular space between the column and condenser, setting up a concentration gradient, with the more volatile components at the top where they are removed.

For the first time, equipment of great fractionating ability has been

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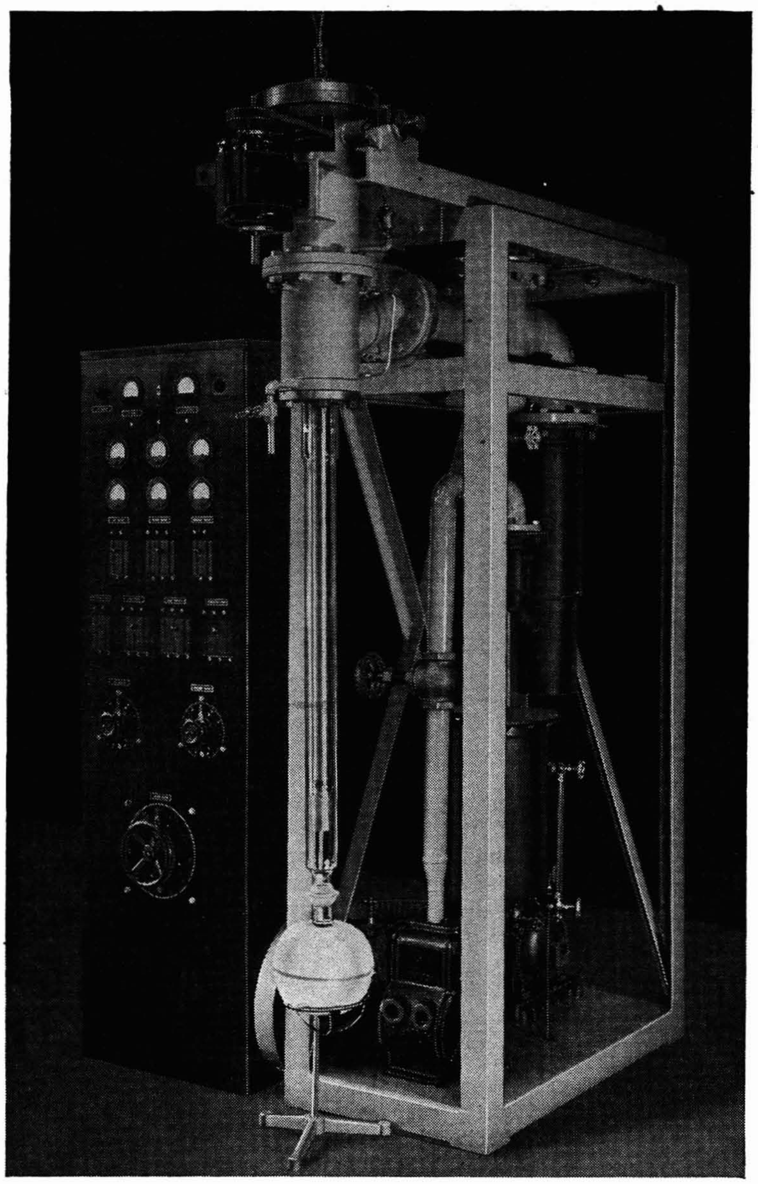

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evolved without introduction of the usual packed column with high impedance to gas or vapor flow.

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For further details, please write National Research Corporation, Cambridge 42, Massachusetts.

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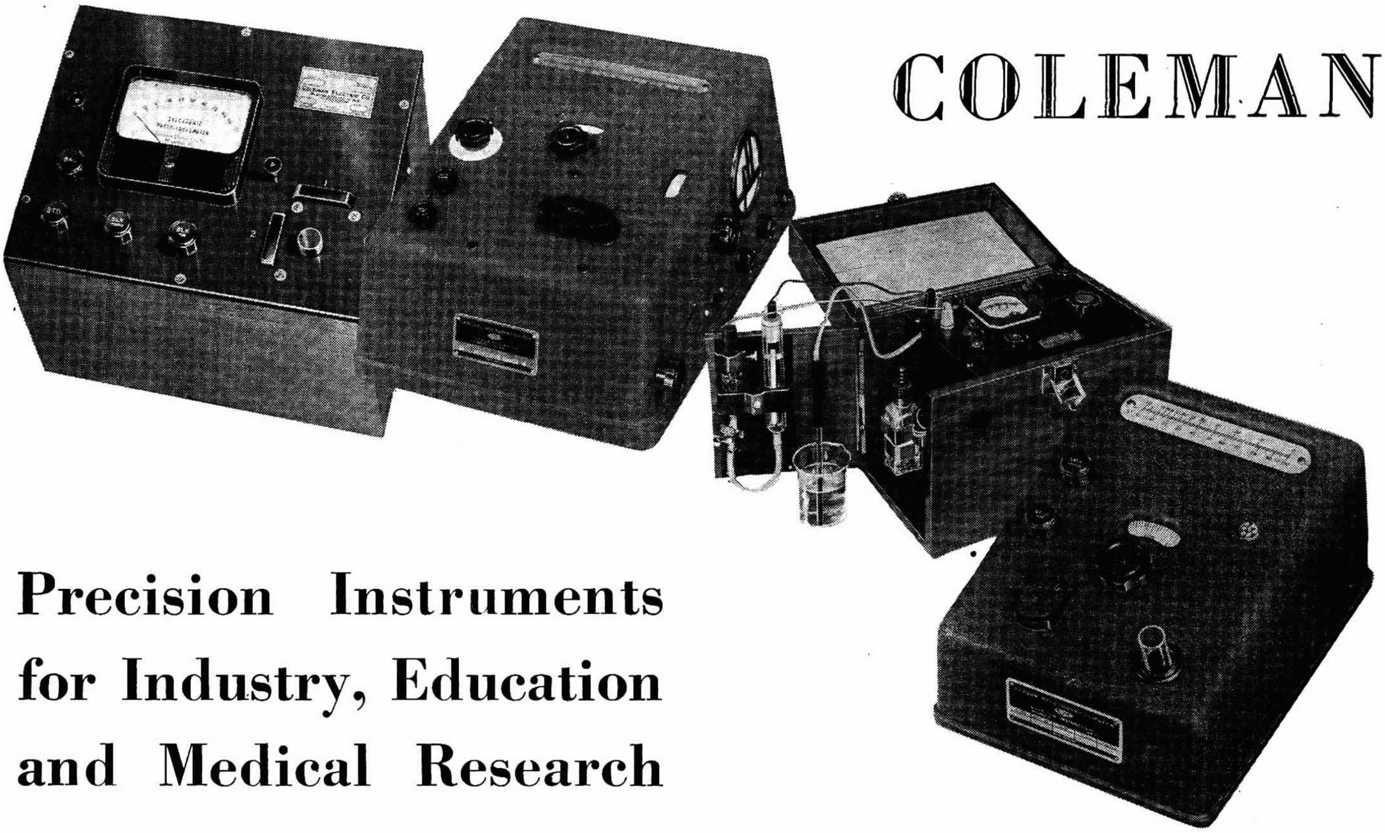

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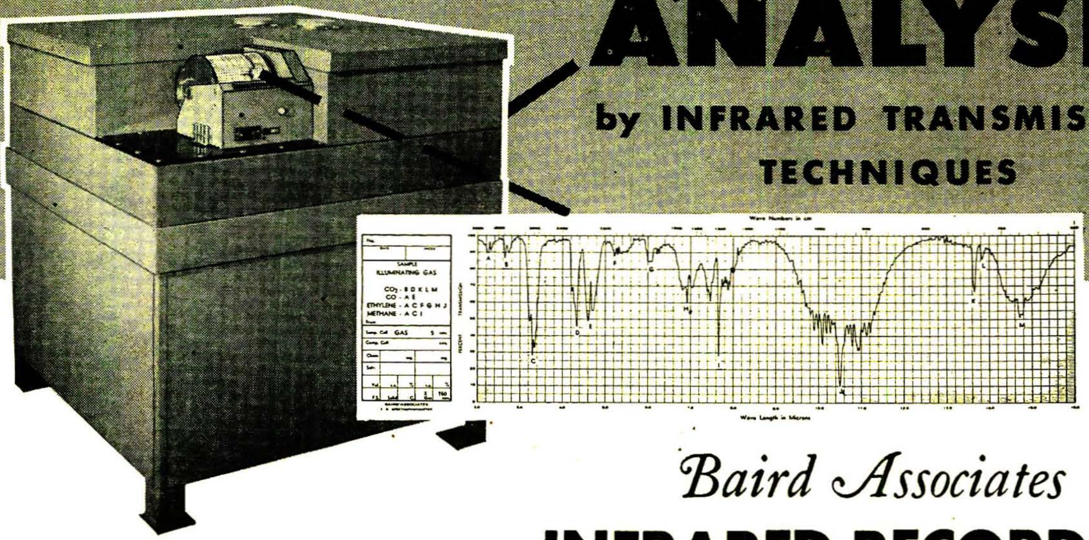

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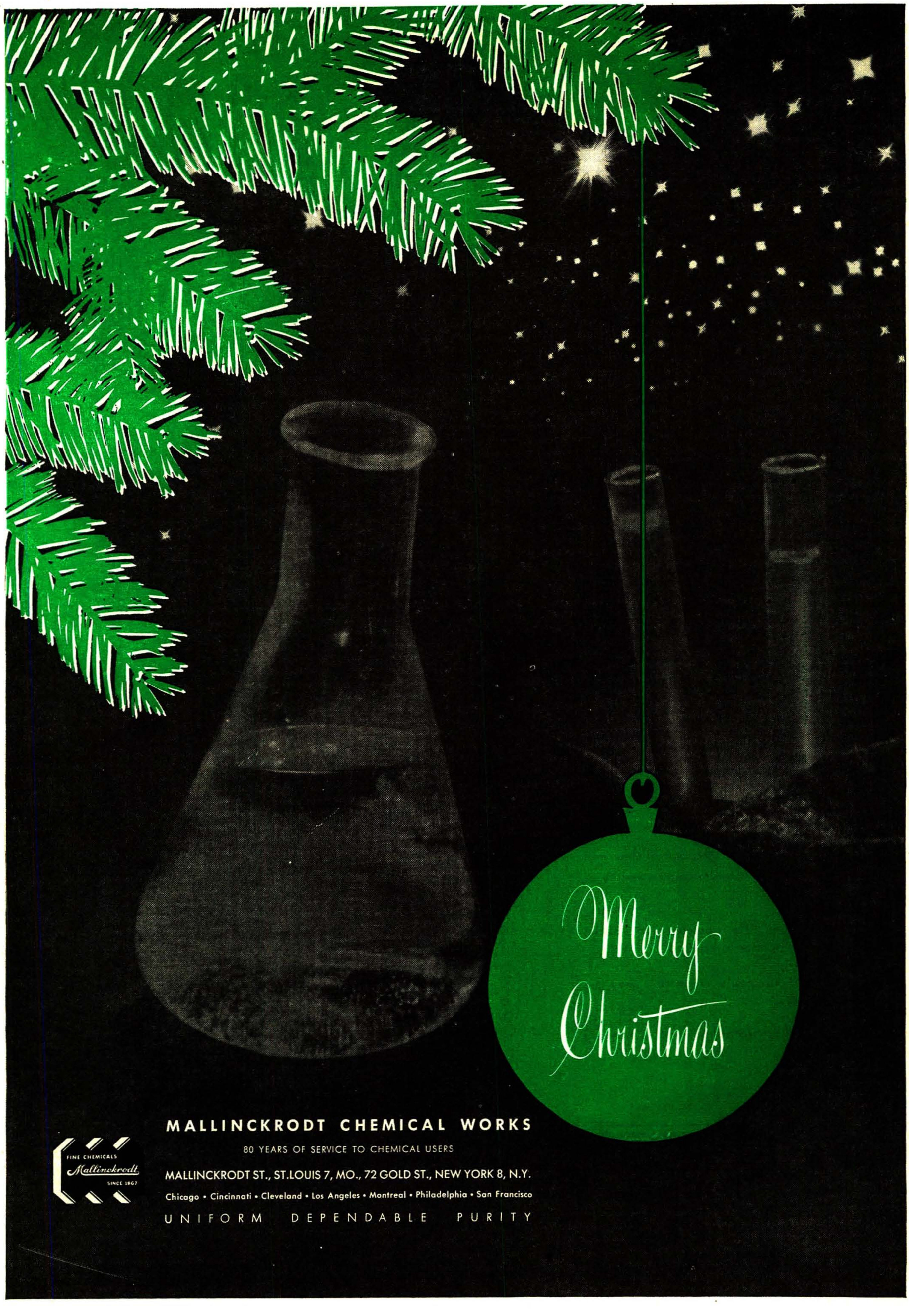
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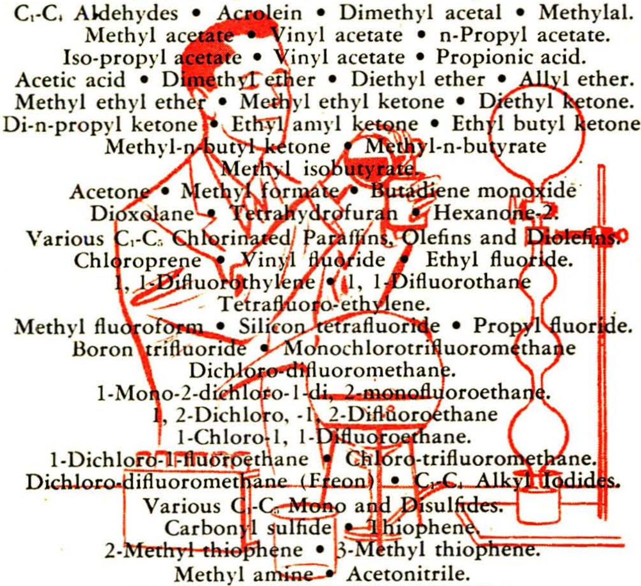

Paraffins, Aromatics, Naphthenes, through C_{10}
Olefins through C_6; some through C_8
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C_1-C_4 Nitroparaffins • C_1-C_4 Mercaptans.
C_1-C_4 Aldehydes • Acrolein • Dimethyl acetal • Methylal.
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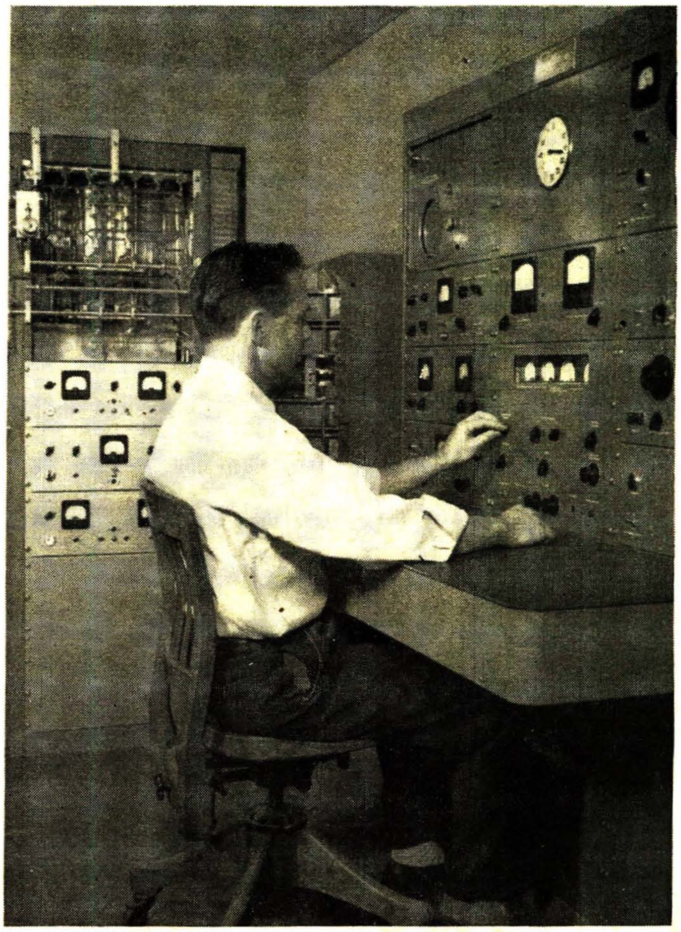

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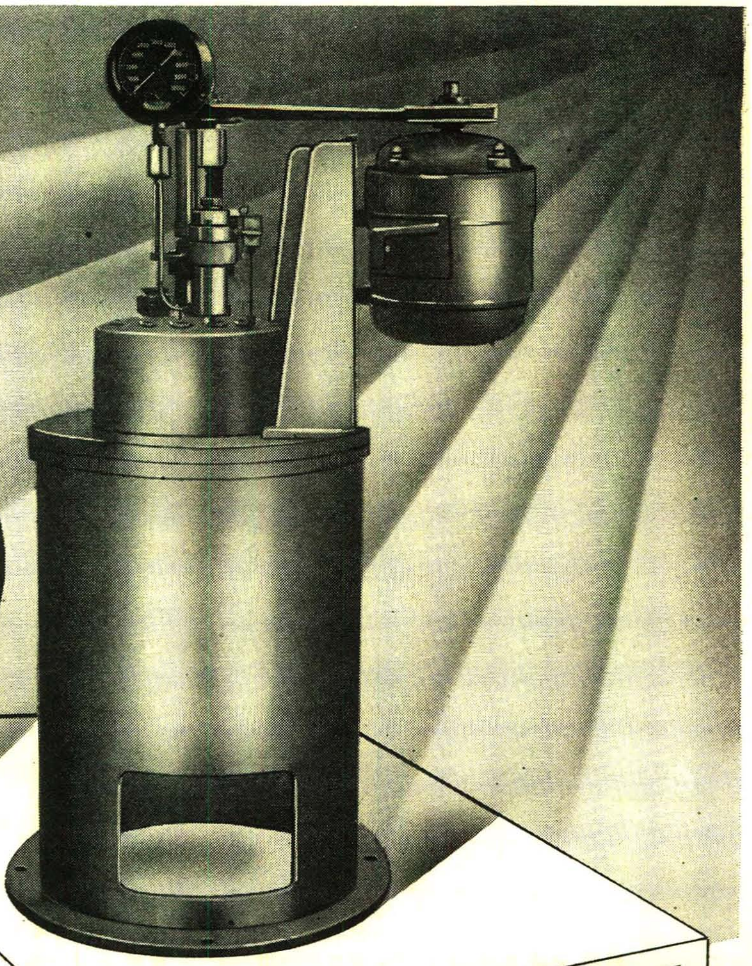

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the analyst's column

THE first four papers published this month were given at the statistical symposium jointly sponsored by the Divisions of Analytical and Micro Chemistry and Industrial and Engineering Chemistry, held at Atlantic City last spring. They cover several subjects and points of view, and the papers with discussion are published, so that the continuity and viewpoint can be maintained for the analyst as well as for those who have interest in the special topics.

ABSTRACTS of papers of interest to analysts from the Eighth Pittsburgh Conference on Applied Spectroscopy are given, beginning on page 1042. Of special general interest to all emission spectroscopists are paper 15 by W. F. Meggers covering the fundamentals and history of spectroscopy and paper 16 which deals with the A.S.T.M. Committee E-2 and its new program of compiling current spectroscopic methods successfully used in industrial and academic laboratories. It is hoped that from this work standardization of methods may come. All progressive men in this field can benefit by cooperating with this important work and sending in their preferred methods.

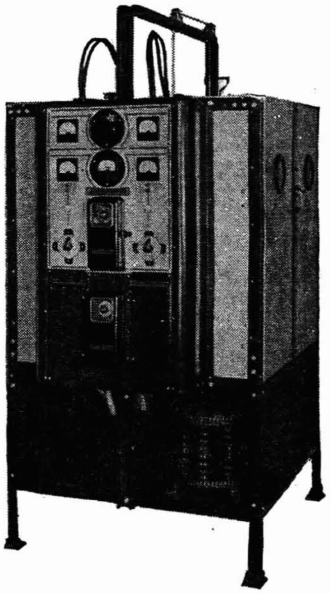
THE Armour Research Foundation, Chicago, Ill., is sponsoring a project for the compilation of crystallographic data of inorganic and organic compounds. Whenever possible it intends to maintain standard reference samples of the material. The punch card system will be used, and it is hoped that others working in this field will also attempt this method of filing their data for ready use. All microscopists, academic or industrial, are asked to contribute data and samples. It is planned to distribute data at definite periodic intervals to each of the contributing laboratories. The data distributed in this way will be almost in the original form. The important compounds for which data are submitted will be checked and completed for formal publication. Credit will be given with each description to the persons and laboratories contributing in any way to the data presented. While one of the most important questions (the conventions to be used in writing the descriptions) has not yet been established definitely, the foundation has adhered in the past to those published by a committee headed by C. W. Mason [IND. ENG. CHEM., ANAL. ED., **17**, 603 (1945)]. Further details can be obtained by writing to W. C. McCrone, a well-known microscopist, who is handling the work for the Armour Foundation. The project has reached the stage where the foundation is ready to receive data as outlined in its proposal.

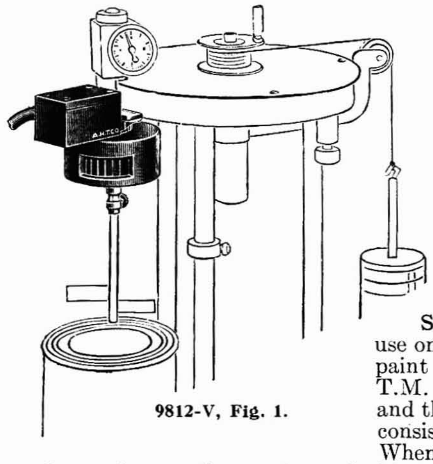
PHILIP W. WEST writes that the symposium at Louisiana State University on modern methods of analytical chemistry will definitely be held February 2, 3, 4, and 5. So far the following have accepted invitations to speak: J. R. Churchill, L. T. Hallett, M. G. Mellon, R. H. Müller, W. J. Murphy, C. E. Starr, and B. W. Washburn.

WE HEAR remarks from time to time on how modern instrumental analysis makes the analyst less and less important. However, as for those of us who must be responsible for developing new methods and wrestling with the problems of separating difficult mixtures and preparing pure standard samples for instruments, our only comment is that modern instruments allow us more time for research. There is a scarcity of top-flight research analysts with broad training and clear heads to cope with the analytical problems of modern science. Instruments in the hands of inferior analytical chemists are definitely a hindrance in the solution of problems where the interpretation of data and a sound appraisal of the proper method of attack are of prime importance.

L. T. Hallett

Associate Editor

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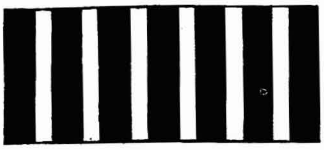

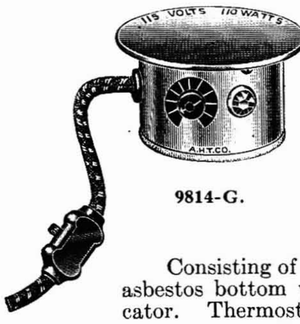
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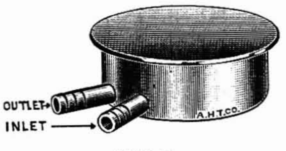
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ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

What Is Analysis? What Is the Role of the Analyst?

In the November issue we published the first in a series of expressions of opinion on the questions: What is analysis? and What is the role of the analyst? It is with pleasure that we present below additional comments from men well known in the chemical field.

R. B. Seymour, University of Chattanooga

Analysis is difficult to define. This is primarily due to the confusion that exists in academic and industrial laboratories and in the minds of the men who are responsible for the operation of these organizations.

In the definition of medicine, the profession of medicine is taken for granted and one does not include first aid or nursing, regardless of their importance. A premedical student who cannot make the grade does not become a routine physician nor does an orderly become a doctor of medicine after he has had six months' experience. Definite spheres of activity have not been established in the field of analysis, which includes the duties of the sample boy as well as the contributions of the world's most outstanding analytical chemist. There is as much difference between analysis as practiced by the routine technician and the analytical chemist as there is between the operations of the physician and the nurse. It is of utmost importance to the entire profession of chemistry that this difference be recognized.

The problem cannot be solved by the substitution of the letter "t" for "is." In order not to increase the confusion it is preferable to discuss the roles of the routine analyst and of the analytical chemist separately. The former is trained to do a specific job, the latter should be educated to be of service to the profession of chemistry.

The modern undergraduate chemistry curriculum should serve to educate rather than train students and should not produce specialists. Such a course should minimize routine and should emphasize instruction in the principles of the science of chemistry. Experiments which illustrate fundamental principles and those which develop laboratory skill can be combined if the instructor is an analytical chemist and not a routine analyst. One must decide whether to use classical methods to train routine analysts who are completely unfamiliar with statistics, spectroscopy, microanalysis, polarography, microscopy, and other tools of modern analysis or to educate creative chemists.

Fortunately, the graduate who has not spent countless hours in titrating, washing, and weighing will not be properly qualified to become a routine analyst. He must choose some other phase of work where he will not be confused with technicians, or further his education by specializing in a major branch of chemistry.

There are many opportunities open to one who has majored in analytical chemistry in an accredited graduate school. He may undertake special analyses, develop new methods, or supervise a group of routine analysts. In no case should he accept a project unless the background of the problem is explained. Otherwise he will be unable to judge the suitability of the sample or the suggested procedure and to decide whether or not the development of procedure modifications is justified. Such work cannot be done by the routine analyst and will merit the enthusiasm of an analytical chemist who knows the problem and can present an intelligent evaluation of the data.

The role of the routine analyst is to follow instructions. The role of the analytical chemist is to ascertain that the instructions are correct and are properly carried out and to make good use of his technical education. If he will assume his proper role he will find it less difficult to prove to himself, his employer, and the routine analysts that analytical chemistry is a profession.

Harold P. Klug, Mellon Institute

Analytical chemistry in its most fundamental aspects is far broader than the mere qualitative and quantitative determination of the elements present in a substance. An increasing array of analytical problems in the larger research institutes and industrial laboratories involves phase identification, polymorph differentiation, stereochemistry (location of groups in the molecule), crystal structure, and other concepts not ordinarily the concern of the routine analyst. In addition, there are all the complex problems attendant on continuous analysis and control in the industrial plant. All these problems legitimately fall within the domain of analysis, but they usually call for a different approach and technique and are likely to require extensive instrumentation. Thus modern analytical chemistry embraces not only routine determination of the composition of substances, but also structural and physicochemical identifications.

Hydrocarbon mixtures, in the past, have been an outstanding analytical problem. Although chemical methods can accurately analyze even those mixtures of components (up to C_4 or C_5) which cannot be separated by fractional distillation, the time required for such an analysis is excessive. Infrared absorption spectroscopy, however, will quantitatively determine seven such components in a mixture with an accuracy of about 0.5% in only one half to one hour. The mass spectrograph, likewise, will do the same analysis in approximately the same time.

In the inorganic field there are many cases which do not lend themselves to the routine methods of analysis. An important example is the determination of quartz in siliceous dusts. In studying the silicosis hazard in industry, analytical methods are needed which will differentiate and quantitatively measure quartz in the presence of other siliceous minerals. A standard method for quartz analysis utilizes the powder method of x-ray diffraction. The powder diffraction pattern of a crystalline compound is a characteristic physical property of the substance, and serves ideally as a "fingerprint" for its identification, even when admixed with other materials. Quantitative methods are based on the relative intensity of the pattern of a component.

A particularly valuable feature of x-ray diffraction methods of analysis is their ability to distinguish between the different allotropic or polymorphic forms of a substance. For instance, rutile and anatase, polymorphic forms of titanium dioxide, are both important in the white pigment industry, but rutile is the more desirable in paints since it has greater covering power, and therefore commands a higher price. These two forms are indistinguishable in routine chemical analysis, but are readily differentiated and analyzed for by diffraction methods.

One of the monumental achievements of x-ray diffraction was the establishing of the structure of penicillin. This was fundamentally an analytical problem, as indeed are all problems of structure determination in newly isolated compounds. Qualitative and quantitative analysis determine the composition of the substance, but this is only half of the problem. The structure, the positions of its atoms, distinguishes a compound from the others isomeric with it.

The complete list of modern physical and physical chemical techniques available to the analyst is large, and has led to a new terminology, "analytical physics." These new tools require specialists for many phases of their application, but their utility and power are making them standard facilities of large research, analytical, and control laboratories. Every research chemist today needs at least a speaking acquaintance with these new tools; otherwise he will not know what important aids they can be in the solution of his problems. The trained analytical chemist, of course, should have a real working knowledge of the entire field of modern instrumental analysis.

The proper training of future research chemists and analytical specialists must emphasize the larger significance of analytical chemistry. Few colleges and universities are prepared to do this job effectively at the moment, but many are cognizant of the problem and are planning instrumentation laboratories. Such laboratories should have associated with them specialists in optical spectroscopy, mass spectroscopy, x-ray diffraction, polarography, and other instrumental techniques if they are to provide anything more than additional elementary laboratory exercises in physical chemistry. The analytical specialist could profit by additional courses in physics, particularly optics and electronics. Finally, a survey type of course in which the various instrumental analysis fields are each discussed in a few lectures by a recognized authority could be very valuable.

Paul D. V. Manning,
International Minerals & Chemical Corp.

ANALYTICAL work and treatment of results obtained form the means of judging and interpreting practically all research and development in all fields of science. Accuracy of results and statistical treatment of such results are therefore of paramount importance. There is also one other factor of equal rank but one which is generally given little consideration in the training of the professional worker. This is the speed of obtaining results.

More often than is generally realized, the position of a corporation in a field of enterprise depends on the speed at which its research and development organization can complete an investigation. The bottleneck all too frequently is found in the great volume of analytical work required.

Because of the greatly increased costs of all types of research, it is also worth while to try to shorten the time required for all operations, but accuracy of results must never be sacrificed.

Our activities in research and development are in many fields—from prospecting thousands of acres of phosphate and potash ores with analysis of thousands of samples for several constituents, through complex organic syntheses where analytical methods must be invented, to the chemical analysis of crops grown in large field agronomy tests where statistical treatment of results is of highest import, and to continuous, round-the-clock pilot-plant operation where the planning of the next day's work depends on analytical results obtained today.

For all these, we have turned to use of new instruments which have usually been developed by physicists and physical chemists. Instruments such as the spectrophotometer, the flame photometer, the polarograph, and others have been of great assistance and have made it possible to discover new phenomena in old fields. The principal difficulty has been in finding men trained in the use of instruments and having a sufficient knowledge of physics to enable them to make applications in new fields. For this, we look for men who are primarily physicists trained in chemistry and mathematics, physical chemists, or those very rare finds—chemists who have had more courses in physics than are given in the usual curriculum. A constantly revised excellent course in instrumental analysis is an essential; additional courses in physics are advisable for all chemists, and a course in statistics is an invaluable aid to any scientific worker.

Edward Wichers, National Bureau of Standards

WHEN the analytical chemist occasionally pauses from the exertion of keeping up with his daily tasks he is apt to wonder what has happened to the dignity of his profession. If he thinks back over the history of chemistry he may ponder sadly that although his scientific progenitors occupied the center of the chemical stage throughout a great part of the nineteenth century, they at last lost the spotlight—first to Kekulé and his tribe, then to Willard Gibbs and his spiritual descendants. While the physical chemist never entirely stole the show from the organic chemist, and more recently has had to share it with still others, the analytical chemist feels in his gloomier moments that for him there is little left but a stage hand's job.

If there is justification for this pessimism, why has the once glorious profession been so debased? In this writer's opinion a major reason is that the analytical chemist too often forgets that he is a chemist and behaves as if he were only a technician. Today we have experts in microanalysis, optical and mass spectrometry, and every other specialized technique one can think of. The analyst is acquiring an easy familiarity with electronic gadgets and is beginning to feel somewhat at home in optics. But too many of us give too little thought to underlying phenomena and to the relation of our activities to the world of chemistry. In the morning we receive a sample about whose significance we do not inquire. In the evening we turn in a report and go home to our supper, little knowing or caring what it all means.

For a large part of the nineteenth century, the major task of the chemist was to resolve the things he saw into their constituent parts—in other words, the analysis of natural materials. Each day brought something new to do that required some new thinking. Today chemistry is mainly concerned with reshaping the materials of nature to suit man's needs, and the analyst must meet the resulting demands for the chemical control of processes and product quality. A large part of his effort must now be spent on providing methods suitable for rapid and repetitive use, the more mechanical in operation the better. The progress made in the development of instrumental methods in the past twenty or thirty years is truly astonishing, and the end is not in sight. These techniques are indispensable, and the analytical chemist must produce them. But they are the product of analytical chemistry and not analytical chemistry itself. This should never be lost sight of, and the distinction should be clearly and insistently brought out in the teaching of analytical chemistry.

If we define the objective of analytical chemistry as the discovery of a sufficient number of chemical and physical phenomena to determine uniquely the presence and concentration of any component (elementary or molecular) of any conceivable chemical system, we see at once that there can be a dignified career for the analytical chemist for a long time to come. Today there is as great a need as there ever was for knowledge of reactions that will serve to identify, to separate, and to determine elements, radicals, and compounds ever more sensitively, more accurately, and more rapidly. To discover them the analytical chemist needs the broadest possible knowledge of chemistry—inorganic, organic, and physical. Of all the family of chemists, he should be a chemist complete, as were his nineteenth century forebears.

If the practitioner, and more especially the teacher, of analytical chemistry will firmly cling to this faith, this branch of our science may hope to regain some of its lost glory.

SYMPOSIUM ON STATISTICAL METHODS IN EXPERIMENTAL AND INDUSTRIAL CHEMISTRY

Introductory Remarks

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TWO convictions have crystallized in the minds of many of us during the last five years or so: (1) Statistical methods of dealing with data have been neglected by the chemist, compared to the manufacturing engineer and the biologist, for example; and (2) modern statistical technique has a great deal to offer in both experimental and applied chemistry.

About the only place in the curriculum where the average chemistry student comes into contact with statistics is in quantitative analysis where the theory or error is considered. Some years ago a prominent statistician and I critically examined a number of standard treatises on analysis with respect to their treatment of error theory. I was shocked to be told by my specialist colleague that none of the authors of these texts seemed aware that anything had happened in statistical theory since 1890!

A very great deal has happened in statistics since that time. However, it is not indeed too great an exaggeration to compare most of our quantitative analysis texts with a treatise on the applications of statistical methods in which the chemistry chapter took no cognizance of the discovery of radioactivity and its sequelae.

In support of the contention that statistics has much to offer us, it can be said that the modern statistical methodologist claims, to the experimental chemist, including the analytical chemist, that he can point out (1) how to design his experiments so as to obtain the most useful body of data; and (2) how to marshal and organize the data so obtained in order that they shall speak with all their potential eloquence. Also, the expert in control charts and related methods tells the manufacturer, the processor, and the packager of chemical products that he can detect the existence of trends that may result in substandard products, earlier than by any other means, so that their causes may be corrected before great harm is done.

So with the conviction that chemistry, although it needed to use statistical methods, was in fact not doing so, Walter Shewhart of the Bell Telephone Laboratories, Grant Wernimont of Eastman Kodak, and I organized this symposium, at the request of the officers of the Divisions of Analytical and Micro Chemistry and of Industrial and Engineering Chemistry.

The general plan is based on two assumptions: that the average chemist in our audience knows very little about statistics; and that a "selling job" has generally got to be done to persuade the management of experimental and production units to try out these new ideas.

The Management Viewpoint

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Various general applications of statistical methods are discussed with particular reference to a number of problems of interest to industrial management. Adaptation of the methods of opinion research to problems in market research is explained. The use of statistics in modern methods of sales forecasting is outlined. Examples are given of the use of statistical methods as a tool in helping the modern business executive adopt a factual approach to problems of marketing, selling, and production planning.

THE layman usually thinks of statistics as involving more or less abstract mathematical considerations. For example, we have heard how astronomers, by application of the theory of error, arrive at a final result of exceedingly small probable error by proper averaging of a very large number of observations, each of which is characterized by a large uncertainty. Or, one may bring to mind the masses of statistics from which some economists are so wont to draw the wrong conclusions. Or, one may recall a cardplayer's estimate of the probability of his drawing a certain card, forgetting that the laws of probability apply accurately only to very large numbers of events. Statistical theory is, of course, very old; but, as with other very old principles, new applications are often only lately discovered. Even in science, many practical applications of statistical theory have only relatively recently been made. Many applications of statistical theory in industry have come even more recently. One of the early applications of statistical theory to practical technical problems was in sampling heterogeneous raw materials. For example, a mathematician can calculate what kind of sample of coal must be taken from a carload in order to achieve a given accuracy in analysis of it as representative of the whole carload, if he knows the maximum variation in composition and the distribution of size of the lumps; and in the application of medical science to the inheritance of blood types, statistical theory is used.

Statistics were applied during the war in the so-called "Operations Research." Statistical methods were used to predetermine the effectiveness of various methods of attack. The methods used in combating the German submarines in the North Atlantic were based on the statistical evaluation of the probability of success—the results proved the validity of the statistical approach. The decision to use mass air attacks over the continent of Europe was made on a similar basis. The strategy employed in attacking Japanese shipping was founded upon the same principle. This whole subject and some of its possible applications to peacetime operations are described by Kittel (*Science*, February 7, 1947).

These and other uses of statistical methods are fascinating in their possibilities and in their results—but let's spend a few minutes on some of the businessman's uses of this technique which is to him a useful management tool.

Market research is today an important phase of business management. No longer does the able businessman launch a new product without predetermining its probability of success. The day has gone by when the executive relies upon intuition or a guess in appraising the acceptance of a new product or the progress of an established product. Instead, he makes use of statistical techniques which have undergone constant refinement and today are surprisingly reliable.

FACTORS IN MARKET RESEARCH

The methods are largely the same as those used in sampling public opinion; as, for example, in the Gallup poll with which many Americans have become acquainted over the last several years. The same basic considerations which determine the success or failure of a public opinion poll also determine the accuracy of the results of market research. The basic considerations are (1) the size of the sample, (2) the character of the cross section, (3) the questions asked and the wording of these questions, and (4) the time factor.

Size of Sample. The first factor, size of sample, seems to be the least understood element in the opinion research field. The average mind tends to associate the accuracy of a prediction directly with the number of persons polled. This association is of such long standing that the real facts have been somewhat obscured. There is, of course, a connection between accuracy and size of sample, but size alone is not the answer to the success or failure of the prediction.

Actually, it is safe to say that no nation-wide poll in the history of this country ever went wrong because too few persons were reached—for example, a survey which predicts an election within 5% is generally regarded as very accurate. Yet the laws of probability show that this degree of accuracy can be attained with from 600 to 900 ballots, if properly selected.

One of the most accurate election predictions made by Dr. Gallup's group included only 2000 cases: the New York State Lehman-Dewey fight of 1942. The final prediction, based on roughly one person out of every 7000 in the population of the state, showed an error of only 0.1%.

Character of Cross Section. The most important factor controlling the accuracy of any opinion survey is the character of the cross section—the way in which the different population groups are balanced in the proper proportions. If the cross section is faulty, no piling up of thousands of interviews in a national survey can eliminate the built-in error. Almost every survey that makes a substantial error goes wrong because the individuals reached do not add up to a representative cross section of the entire population.

In determining the size and character of a market research sample, initial consideration is usually given to the geographic scope of the survey. Depending on the distribution of the company's product and the particular problem at hand, the survey may be national or sectional. Even with national distribution of a product, certain problems—such as questions on package design—may be answered by a reasonably limited consumer investigation.

A second factor influencing composition and size of the sample is the question of whether men or women buy the product. Who actually uses it? Does someone other than the actual buyer control the final decision as to the particular product purchased? The survey should reach those who make the final decision on purchasing. Most market research on consumer goods is directed at the housewives, since in this country they are—as a group—more important than men in giving the final word as to which product is bought.

Another factor of prime importance is the extent to which the data must eventually be broken down. Breakdowns may be necessary by geographic area, economic status of the respondents, city-size groups, urban versus rural areas, age, sex, education, or other divisions. The sample must be larger if results are to be broken down than if no subgroupings are necessary. Final determination of the sample size will depend on the error allowable in the smallest subdivision.

Still another consideration in deciding on the size of sample to be used is the proportion in which opinions, habits, or preferences are believed to be divided. If it is expected that results will show a definite tendency in one particular direction, the sample can be smaller than if no such tendency is likely. If this expectation is not borne out by the preliminary findings, additional interviews may be necessary to decrease the probable error and determine more accurately the relative standing of any closely balanced opinions or preferences. The safest course would naturally be to assume at the beginning that results will be almost evenly divided and plan accordingly to use as large a sample as practicable, so that the probable error will be small.

In setting up the sample requirements for a market survey, these factors and other product considerations must be closely analyzed. An understanding of the application of basic statistical rules must be combined with knowledge of the particular product field involved to assure satisfactory composition and size of the market cross section.

The Questions. When the size of sample necessary for a survey has been determined and the cross section selected, the next problem is the framing of the questions themselves. Every question must be worded clearly, simply, and without bias.

It has been proved over and over again that, in any sort of research dealing with people's opinions, experience in preparing the questions to be asked cannot take the place of actually testing the questions on a number of people before the full-scale survey is made. In addition to the pretesting of questions, organizations engaged in opinion research frequently utilize a simple device for measuring the effect of phrasing in the survey itself. Two wordings of a question are prepared and printed on different questionnaire forms—A and B. The A form is put to half the people in the cross section, and the B form to the other half. Both halves contain the same types of people. The tabulation soon reveals the difference, if any, which is caused by the wording. If the difference is greater than the expected variations due to size of sample, then new and more neutral phrasings are found and substituted. Thus, even the wording of questions in opinion research is subjected to statistical scrutiny.

Timing. The timing of a market survey may be vitally important if the product under study has a seasonal market. Here again the specific purpose of the survey will be a controlling factor. The survey may be of a continuous nature, designed to measure the seasonal influence or to determine its cause, or it may be one of a series of annual market studies to measure the yearly trend in product use or brand standing. If this is the purpose, each successive survey has to be conducted at approximately the same time of the year in order to eliminate the seasonal influence. Unless seasonal conditions during the field investigations each year are comparable, statistical data on the annual trends are likely to be of little value.

CASE HISTORIES

Here are three quick case histories to show how market research has been used in specific instances.

Soap. Our first concerns a soap manufacturer who developed a new toilet soap and was anxious to put it on the market. Laboratory tests and home-use tests by his employees had convinced him that his new product was good. But the money needed to put across a new soap product is substantial and our soap manufacturer was aware of this. He wanted to know that his new soap would appeal to housewives. So he turned to consumer research.

Here are the points on which this manufacturer sought the housewives' opinions: What should the soap be named? What should the wrapper look like? How big should the cake of soap be? Was the perfume right? How sudsy should the soap be? What premiums would be most likely to influence women to buy the soap for the first time? There were other questions involved, but this will give you an idea of the range of information this soap manufacturer was after.

As a result of 14 separate consumer surveys, it was found that the soap still needed to be changed in certain respects to give it the greatest market appeal. When these changes were made and the product was finally launched on the market, its success showed that the time and expense involved in this manufacturer's very thorough consumer research program had been an excellent investment.

Household Product. Here is another case where consumer research was successfully employed. The X Chemical Company became interested in purchasing a brand-new type of household chemical product from the small concern which had developed it but was not equipped to handle its distribution. Although X felt optimistic about the product, it was so entirely different from anything on the market that there was no factual assurance it would sell in any volume. Therefore, before committing itself to buy the product, the X company decided to study the market and find out from a cross section of housewives whether or not such a product would be really acceptable to them.

With the help of an outside market research organization, X went to housewives in different parts of the country, supplied them with samples of the new product, and then sent interviewers to get their reactions after they had had time to use the product.

This, in brief, is what they found out: In very low-income homes the housewives considered the product more of a luxury than a necessity. Except for this group, however, the majority of women were honestly enthusiastic about it. The X company decided to purchase the product, and subsequent sales have shown that the decision, based on consumer research, was well advised.

Baby Lotions. Here is a case where Johnson & Johnson used consumer research with a type of product which was new not only to us but to the entire baby products field. Three or four years ago we perfected a new baby lotion which we personally felt had certain advantages over the baby oils generally used. Our laboratories had done a thoroughly excellent development job. The product formula was well suited to volume production. The mothers among our employees and in their families tried it and liked it. But we still needed to know how mothers in general would receive this new item.

In 1944, with the cooperation of our advertising agency, we distributed samples of the new lotion to well over 1000 mothers of babies less than a year old. We asked each mother to give the lotion a three-week trial. At the end of this period, we interviewed the mothers to get their honest opinions of the lotion. We didn't expect to get a 100% favorable reaction to the product. You cannot please everybody, and if the results had been 100% favorable we wouldn't have believed them. But we did find that an overwhelming majority of the mothers were enthusiastic about the new lotion. Through lengthy questioning of each mother, we found that this enthusiasm was perfectly genuine and not the result of being given something for nothing.

Several months after this survey Johnson & Johnson's baby lotion was introduced to the national market. Sales experience with it since that time has verified again our confidence in properly planned consumer research.

EVALUATION OF SALES POSITION

After a product is launched, it is manifestly important to know what sales progress is being made—nationally, sectionally, and otherwise. With the return of competitive conditions in the selling field, renewed attention is being given to the use of statistical methods in evaluating one's sales position. In years past, sales executives relied in the main upon the collection and interpretation of a company's own internal statistics. Any business, regardless of size, has available through its basic records of production, sales, and expenses, a wealth of information concerning its own past and present sales pattern. Sales have been tabulated by product, by geographical area, by size of account, by type of outlet, and so forth. The results of the analyses of such internal material have been restricted mainly to ratios, to averages, and to the comparison of sales in one area with another or between types of outlets. Statistics of this nature will throw light on many problems, such as distribution costs, improper emphasis on unprofitable products, and lack of adequate coverage in the field.

Fortunately, during the period when business has been improving its own sales records, a vast supply of information on general economic activity has been made available. Current reports from government, trade associations, and private organizations supply facts about total industry sales, total retail sales, the consumer, competition, sectional and local market data, and national buying power.

In so far as general statistical data are concerned, an important problem facing management is the selection of the proper measure of potential sales and the methods to be used in correlating such information with the company's sales. It is essential that we have some yardstick to measure the level of sales performance—in total and by-products, markets, and sales territories. For most consumer products the over-all measure of national purchasing power, perhaps combined with population statistics, represents the best single measure of demand. Such an index takes into consideration the number of people and families with money to spend. Through the comparison of a company's past sales with total buying power and other factors, it is possible to determine, with a fair degree of accuracy, the volume of sales possible for any given level of national buying power. The results obtained by such statistical methods, while by no means as accurate as those possible to the research technician or chemist, are invaluable aids to management, which is faced with the problem of determining sales potentials of existing products and possible markets for the new products developed by the research department.

Too often the measure of the potential market is based upon statistical data which are not available until several months after the close of a year. While such an index can be used to measure past performance, it is of no assistance in scheduling future production, forecasting future sales volume, or setting up quotas for the sales personnel. An index of potential sales is of far greater value if the basic data, such as buying power, can be determined in advance. Despite the obvious difficulties that such forecasting entails, the problem is by no means hopeless. Certain economic activity precedes other activity and the careful use of such information can be made to yield reasonable forecasts of buying power.

There is a series of events which has at one time or another anticipated business activity. In the past, the stock market generally anticipated changes in production by three to six months. Changes in industrial production in turn generally preceded changes in retail sales by several months. In recent years, a better measure of economic activity has been gathered which to date has consistently preceded changes in business generally. This is the compilation of orders received by manufacturers, better known as new order series. Swings in the business cycle have generally been characterized by wide fluctuations in the production of capital goods and little fluctuation in the production of consumer goods. New orders for capital goods generally take anywhere from three months to two years to fill as, for example, orders for locomotives, generating equipment, and related items. When orders for all goods are combined into one index to weigh properly the importance of each type of goods, as is done in the new order series published by the Government and others, such indexes tend to anticipate general business activity and national buying power by from three months to a year. Naturally, such indexes must be used with reservation, for other factors influence our national well-being besides the volume of orders being received by manufacturers. Changes in the Federal Reserve policy can greatly influence the supply of funds available to business to finance production. Government expenditures and receipts can also have their influence on business activity. Once such different business indicators have been skillfully blended into one economic entity they can be used to project national income for a number of months ahead. We leave to the economist the problem of going behind such indicators to find the basic causes generating the ups and downs of the business cycle.

Once a forecast of national income is available, it is no easy solution to stick to it. In the past two years, the country has been deluged with dire predictions and optimistic eulogies at one and the same time and it is difficult to stick to the known facts and ignore the unfounded rumors which circulate daily. But gradually the science of forecasting economic trends is developing and each year we are better able to chart our future course.

Through one of the companies which specialize in such economic forecasting, it is possible to secure forecasts of national income broken down by states and counties. Such information permits one to anticipate sales level by as much as a year in advance, and thus to set up production, promotion, and merchandising plans in full preparation for the expected demand. The forecasts are, of course, not infallible—but the statistical approach is more reliable by far than unsupported guesses of what the future holds. The estimated national income for the United States for the year 1947 is $179,000,000,000 dollars as compared with $165,000,000,000 for 1946, and $70,000,000,000 for 1939. A change in national income generates different degrees of change in the demand for different products. The process whereby a 10% increase in income produces a 6 to 10% increase in the demand for drug products becomes clearer if we examine more closely the distribution of income and the demand for products by different income groups.

A family having an income of say $3000 a year tends to spend twice as much on drug products as a family with an income of $1500. This same family will, as a group, however, spend three or four times as much on an automobile and other luxury products as will the family of lower income as a group. Little of the extra income will be spent for the basic necessities of life and more will be available for other goods.

At the present time about half of the families in the United States have incomes of $2000 or better. As national income increases by 10%, a number of the families in the lower brackets will move into the upper brackets and as a result will be able to increase their purchase of goods accordingly. Their purchases will change in character from that of lower income to that of a higher income family. Thus the changing level of national income is reflected in the changing demand for various products.

When the national income or buying power level in detail by counties is available, it is possible to compare the sales performance in each sales territory with the average for all territories or with the company goal. Such a comparison immediately points out strong and weak major markets, where additional sales effort will pay dividends, and definitely indicates the value of the sales representative. Knowing the buying power in the immediate future by areas tells where the company should expect the greatest increases and may help explain why certain areas increase faster than others. For example, one of the largest factors contributing to the expected national income for 1947 is agricultural products. The forecast 1947 national income shows the largest gain to be in agriculture and lumbering sections of the United States.

The pace is swift under the competitive system that we enjoy in America. With little or no regimented control, deserved success comes to the businessman who is able to outthink, outproduce, and outsell his competitors.

There is a premium upon brains and the intelligent use of facts. Naturally the American businessman is vitally interested in statistical techniques. In the evaluation of new products, in the analysis of sales performance, in the selection of personnel and its proper placement, in production, in quality control, and in a host of other ways we have employed statistical methods with increasing success.

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Technique for Testing the Accuracy of Analytical Data

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A new or modified quantitative analysis procedure is usually tested over a range of sample size or amount of substance sought. Frequently such data, when plotted, should give a straight line through the origin. Several examples of published analytical data have been utilized to illustrate a statistical technique for determining whether the line may be considered to pass through the origin and to point out the advantage of using the slope of the line as a check on the analytical method.

An increasing number of chemists are finding statistical methods useful in their work. It is now customary to report, along with the arithmetic average, either the standard deviation of the individual measurements or the standard error of their average. Besides the arithmetic average or mean there are other important statistics. Among these are the slope and intercept, two constants in the straight line fitted by least squares to a series of paired values. Appropriate formulas exist for the standard deviations of these two statistics, although little use has been made of them by chemists. The present paper is concerned with showing that the slope, as a statistic, has a wide field of application in analytical chemistry. After a statement of the principles involved several examples are discussed, using data taken from the literature.

In the process of working up a new quantitative analytical procedure it is customary to take a number of samples and determine for each sample the amount of substance sought in the analysis. For example, in determining the atomic weight of iodine a number of samples of silver are taken and the corresponding weights of silver iodide found. As a result a series of paired values is available. In the atomic weight determination the ratio of iodine to silver may be computed for each pair and the average ratio computed. These pairs may also be used to plot a series of points and, if the weights of silver cover a sufficient range, the points determine a straight line which should pass through the origin. When the slope and intercept of the straight line have been found, a physical interpretation is at hand for each. Should the line not pass through the origin, it will intercept the y axis at a value corresponding to the blank determination for the chemical analysis.

The other constant, the slope, is the change in iodine corresponding to one unit of silver. This is precisely the value sought in the customary computation of the iodine to silver ratio. The estimate of this ratio obtained from the slope is independent of any constant errors in the chemical analysis because a constant error will raise or lower all the points the same amount without altering the slope. Disagreement between the ratio as customarily computed and as computed from the slope is a warning signal for the analyst. Naturally, to make an intelligent judgment concerning any discrepancy found between the two estimates, it is necessary to compute standard errors for them. Fortunately, this involves little computation in addition to that required to fit the line by least squares. The estimation of the standard deviation is based upon the deviations of the plotted points from the fitted straight line. This requires that the relationship be linear and that the x values be either without error or with errors small in comparison with the y values. The necessary computations are set forth below.

COMPUTATIONS FOR INTERCEPT AND SLOPE AND THEIR STANDARD DEVIATIONS FOR STRAIGHT LINE $Y = a + bx$

Sample	x	y	x^2	xy	y^2	Y	$y - Y$	$(y - Y)^2$
1	.	.	.	.	.	.	.	.
2	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
n	.	.	.	.	.	.	.	.
Total	Σx	Σy	Σx^2	Σxy	Σy^2	Σy	0	$(n - 2)s^2$
Av.	$\bar{x}$	$\bar{y}$						

$$\text{Slope} = b = \frac{n\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

$$\text{Intercept} = a = \bar{y} - b\,\bar{x}$$

$$\text{Sum } (y - Y)^2 = \Sigma y^2 - \bar{y}\Sigma y - b(\Sigma xy - \bar{x}\Sigma y) = (n - 2)s^2$$

$$\text{Standard deviation of single analysis} = s = \sqrt{\frac{\Sigma(y - Y)^2}{n - 2}}$$

$$\text{Standard deviation of intercept} = s\sqrt{\frac{\Sigma x^2}{n\Sigma x^2 - (\Sigma x)^2}} = s_a$$

$$\text{Standard deviation of slope} = \frac{s}{\sqrt{\Sigma x^2 - \bar{x}\Sigma x}} = s_b$$

$$t_{\text{intercept}} = \frac{a}{s_a} \text{ with } (n - 2) \text{ degrees of freedom.}$$

Consult probability tables of t (*3*, *7*).

The computations thus far determine the intercept and slope in the equation for the straight line and the standard deviations of the two statistics. The last three columns serve as checks. The sum of the computed Y values should equal the sum of the observed y values. The sum of the squares of the differences between observed and computed values, $(y - Y)^2$, may be computed directly as in the last column of the table or from the formula in the third line below the table. This sum is equal to $(n - 2)s^2$, where s is the estimated standard deviation of a single analysis.

The foregoing computations are more tedious than the customary practice of computing the ratio of y to x for each pair and taking the average of these ratios as the best estimate. The slope, b, will generally give a different estimate of this ratio and it is worth considering how this comes about. The practice of taking the average of the individual ratios assigns equal weight to each ratio regardless of the size of the sample. This is to be recommended when the analytical errors increase proportionately with the size of the sample. On the other hand, the estimate based upon the slope, b, assumes that the analytical errors (actual magnitude, not percentagewise) are not influenced by sample size, x, over the range of sample sizes involved. Also, the effect of a blank or other contamination which is independent of the sample size will be eliminated in the computation of the slope, but not in the average of the individual ratios.

The question is not entirely one of choosing between these alternative methods of estimating the ratio of y to x. It is true for a line passing through the origin that the ratio of y to x is the slope of the line. Thus, for data which do put the line through the origin, the computed b will be in agreement with the average of the individual ratios of y to x. We may conclude, therefore, that it is the occurrence of a disagreement between b and the average of the individual ratios which reveals a state of affairs that might pass unsuspected if only the average of the individual ratios is computed. It will rarely be the case that b and the average of the ratios agree exactly. They should not be combined. If there is a considerable difference between them it will be revealed by computing t for the intercept, in which case additional data should be sought to explain the discrepancy.

The computation of b makes use of information that is not utilized when only the individual ratios are computed. Computing the ratio of y to x in effect reduces all samples to the same size and does not use the information made available by having samples of different sizes. Plotting the points determined by the paired values and fitting the straight line permits a test to determine whether the line may justifiably be considered to pass through the origin. Taking the average of the individual ratios merely assumes that the line goes through the origin.

An alternative and more elegant statistical test to determine whether the data determine a line which may be considered to pass through the origin is based upon computing the sums of squares of residuals, S' and S, after fitting both $Y' = b'x$ and $Y = a + bx$. Then $(S' - S)(n - 2)/S$ is t^2 with $(n - 2)$ degrees of freedom. It seems desirable to introduce the notion of using the slope without undertaking an exposition of the analysis of variance.

ILLUSTRATIVE EXAMPLES

1. As a representative case of high-precision chemical analysis some data from an atomic weight determination of iodine (*1*) will serve to illustrate an instance of agreement between the average ratio and b.

In commenting upon these data it should be pointed out that the x values are supposed to be without error. In practice this means that the x values must have definitely smaller errors than the y values. This is certainly the case here where the silver is merely weighed, but the weight of iodine involves the chemical reaction, washing, filtering, drying, and weighing. The straight line intercepts the y axis at about 0.5 mg. This is less than the standard deviation of the intercept and as far as these data are concerned the intercept would differ by as much as 0.5 mg. from zero four times out of ten. The relatively large standard deviation for the intercept is due to the rather small range in silver weights. If the spread had been over a range of 6 or 7 grams instead of 2 and the value of s remained the same, it is possible that an intercept of 0.5 mg. would have been found to be beyond the reasonable limits of acceptance. It is not difficult to see that the more extensive the range over the x axis the more certainly will the slope and intercept be determined for any given number of samples.

It is of interest that five different silver preparations and two iodine preparations were used in the 16 analyses. The silver and iodine preparations were used in the combinations shown in Table II.

Table I. Atomic Weight Determination of Iodine

	Silver, Grams x	Iodine, Grams y	Ratio
	9.11927	10.72811	1.176422
	10.48742	12.33766	1.176425
	10.14331	11.93258	1.176399
	9.00775	10.59708	1.176440
	9.53995	11.22338	1.176461
	9.78621	11.51298	1.176449
	9.04011	10.63499	1.176423
	9.99801	11.76207	1.176441
	9.14163	10.75438	1.176418
	10.00740	11.77284	1.176413
	10.47710	12.32578	1.176450
	9.52800	11.20913	1.176441
	9.89577	11.64167	1.176429
	10.47841	12.32701	1.176420
	10.44012	12.28214	1.176437
	8.47813	9.97414	1.176455
Total	155.56859	183.01594	18.822923
Av.	9.7230369	11.43849625	1.17643269

$a = 0.00053590$

$(n - 2)s^2 = 39.0 \times 10^{-8}$

$s = 0.000167$

$s_a = 0.000668$

$b = 1.17637735$

$t_a = 0.804$

for $t = 0.868$ $P = 0.40$

Table II. Silver Preparation

Iodine	A	B	C	D	E
I	22 25	41 41	29 20 37	49 50	55
II	−1 40 18	23 13	..	61	..

The entries are the individual ratios diminished by 1.176400 and multiplied by 10^6. Two combinations were not tried. Possibly the available amounts of the different preparations dictated the above selections. Every statistician will regret that it was not possible to arrange for two analyses for each of four silver preparations with two iodine preparations. It would be easy then to search for differences among the silver preparations, to contrast the two iodine preparations, and if there appeared to be a difference between the iodine preparations, to see if it were consistent over the four silver preparations. The statistician would make an analysis of variance (*2*, *7*):

	Degrees of Freedom	Mean Square (Variance)
Between silvers	3	...
Between iodines	1	...
Interaction	3	...
Between duplicates (within combinations)	8	...
	15	

Four estimates of the variance (square of the standard deviation) are available and the first three may be appraised in terms of that based on the duplicates.

As the data stand it would be a great deal of trouble to go beyond the following division:

	Degrees of Freedom	Mean Square (Variance)
Between combinations	7	458
Within combinations	8	131

The ratio of these is known as F, here equal to 3.5 and just at the 5% level of significance. The evidence is suggestive of differences between the preparations and if the analyses had been distributed evenly the chances are that the source of disturbance could have been narrowed down considerably.

2. At the other extreme from atomic weight determinations a rapid control method for fat in meat (*6*) resulted in some data which show a disagreement between the average ratio and b. Twenty samples were analyzed by both the proposed method and the A.O.A.C. method (Table III). A column of ratios has been added and the samples have been rearranged in ascending order of fat content. The following values will be helpful in repeating the computations:

$$\Sigma x^2,\ 19710.67$$
$$\Sigma y^2,\ 19656.03$$
$$\Sigma xy,\ 19679.30$$

In making computations which involve taking the difference between two large numbers, care must be taken to carry sufficient places. A computing machine is almost indispensable for the atomic weight data in the preceding example.

The rearrangement of the data in order of increasing fat content and the column of ratios already suggest certain shortcomings in the proposed method. It is apparent that samples of low fat content give high results and samples of high fat content run low. It is of interest to compare the various estimates of the ratio of fat found by the rapid method to fat found by the official method. As computed by the usual method of taking the average of the 20 individual ratios, the new method appears to run high. The slope shows a marked disagreement with the ratio of unity. The equation, $y = 1.05 + 0.9663x$, confirms what is apparent on close inspection of the data. The value obtained for t shows that, in the present state of development of the method, the line cannot be considered to pass through the origin.

In the absence of anything to the contrary, the discussion has assumed that the official method is accurate. There would have been some advantages in choosing 10 instead of 20 samples and running duplicate determinations by each method of analysis. This would have fixed the x values more precisely and would also permit an examination of the data to see if the standard deviation as estimated by the deviations from the straight line was consistent with an estimate based on the duplicates. There would have been no need to run a separate series for reproducibility.

3. A more typical example of analytical chemistry is furnished by a proposed method for calcium in the presence of large amounts of magnesium (*4*). Ten different samples containing known amounts of calcium oxide were analyzed by both the old and new methods.

Table III. Comparison of Modified Babcock Method with Standard A.O.A.C. Method

	A.O.A.C. x	Babcock y	Ratio
Wieners	22.0	22.3	1.0136
	22.1	21.8	0.9864
	22.1	22.4	1.0135
	22.2	22.5	1.0135
Chopped ham	24.6	24.9	1.0121
Chopped pork	25.3	25.6	1.0118
Chopped ham	25.3	25.8	1.0197
	25.6	26.2	1.0234
	25.6	26.1	1.0195
	25.9	26.7	1.0308
Wieners	26.0	26.3	1.0115
	26.2	24.9	0.9503
	27.0	26.9	0.9962
Chopped ham	27.3	28.4	1.0402
	27.7	27.1	0.9783
Pork sausage links	41.5	41.4	0.9975
	41.6	41.4	0.9951
Bulk pork sausage	45.5	45.5	1.0000
	48.5	48.2	0.9938
	49.1	47.5	0.9674
Total	601.1	601.9	20.0746
Av.	30.055	30.095	1.00373

$a = 1.0527$ $\qquad b = 0.96631$

$(n-2)s^2 = 6.2009;\ s_a = 0.455;$ $\qquad s_b = 0.0145$

$t = \frac{a}{s_a} = 2.32$, 18 degrees of freedom; $\quad t = 2.10$ for $P = 0.05$

Taking the known calcium oxide content of the samples as the x variable, a straight line has been fitted for both the old and new methods. A comparison of the statistics for the two methods reveals that the average ratio and b are in much closer agreement for the new method and that the new method has the smaller standard deviation. The values for t indicate that both lines may be considered to pass through the origin, although t is rather large in the case of the old method.

Table IV. Gravimetric Determination of Calcium in Presence of Magnesium

		CaO Found			
	CaO Present	Old Method		New Method	
	Mg.	*Mg.*	Ratio	*Mg.*	Ratio
	4.0	3.7	0.925	3.9	0.975
	8.0	7.8	0.975	8.1	1.013
	12.5	12.1	0.968	12.4	0.992
	16.0	15.6	0.975	16.0	1.000
	20.0	19.8	0.990	19.8	0.990
	25.0	24.5	0.980	25.0	1.000
	31.0	31.1	1.003	31.1	1.003
	36.0	35.5	0.986	35.8	0.994
	40.0	39.4	0.985	40.1	1.003
	40.0	39.5	0.988	40.1	1.003
Total	232.5	229.0	9.775	232.3	9.973
Av.	23.25	22.90	0.9775	23.23	0.9973
$b =$		0.994757		1.002359	
$(n-2)s^2 =$		0.3419		0.1273	
$s =$		0.207		0.126	
$a =$		−0.2281		−0.0748	
$s_a =$		0.138		0.084	
$t =$		1.65		0.89	

The authors give some additional data showing ten analyses by each method on the same sample of magnesite. This is presumably to show the precision of the methods. It would have been more advantageous to run two analyses by each method on the ten samples listed above. The ten pairs would then furnish an independent estimate of the standard deviation as will be pointed out in the next example.

The ten analyses performed on a sample containing 26.8 mg. of calcium oxide gave the following results:

		Old Method	New Method
		26.2	27.4
		26.6	27.2
		26.1	27.4
		26.1	26.9
		26.2	27.3
		26.4	26.4
		26.5	26.2
		26.0	26.9
		26.0	27.0
		26.1	27.1
	Av.	26.22	26.98
	s	0.210	0.405
Compare with s computed from deviations from straight line	s	0.207	0.126

In the case of the old method the standard deviation as calculated from the ten analyses agrees very closely with the value 0.207 based upon the deviations of the points from the straight line. It is disconcerting, however, to find that for the new method the series of ten analyses gives a much larger estimate of s than that found above. The difference is great enough to warrant explanation.

4. In a study of the antimony electrode Hovorka and Chapman (*5*) published some data which have several interesting characteristics. For seven different solutions, covering a range in pH from 2.20 to 8.00, they recorded the voltage across antimony and hydrogen electrodes. Their results are shown in Table V. They conclude that apart from a large deviation for pH 8.00 the voltages may be considered constant and they arrive at 255.2 mv. as an average value.

Table V. Observed Voltage across Antimony and Hydrogen Electrodes

pH	Set *a*	Set *b*	Av.
	Millivolts		
2.20	255.38	255.34	255.36
3.00	255.12	255.12	255.12
4.20	255.09	255.10	255.10
5.00	255.01	255.00	255.01
6.00	255.61	255.41	255.51
6.80	255.91	255.74	255.83
8.00	256.71	256.72	256.72

These data differ from preceding examples, since the best line through the points should have zero slope and the intercept is the constant sought. It will reduce the arithmetic as well as reveal the character of the measurements if the above voltages are all reduced by 255 mv.

Table VI. Coded Data from Table V

					Calculated Values		
	Observed Values				Omitting pH 8.0		All points, curve
pH	Set *a*	Set *b*	Diff.	Av.	Line	Curve	
				Hundredths of Millivolts			
2.20	38	34	4	36.0	8.2	36.4	36.5
3.00	12	12	0	12.0	16.4	12.5	12.5
4.20	9	10	1	9.5	28.5	2.1	2.0
5.00	1	0	1	0.5	36.7	12.2	12.1
6.00	61	41	20	51.0	46.8	43.8	43.9
6.80	91	74	17	82.5	54.9	84.5	84.6
8.00	171	172	1	171.5	...	(170.9)	171.4

More interesting than the out-of-line value for pH 8.00 is the very evident trend in the whole set. The averages fall off smoothly to a minimum and then increase in such a way as to suggest that the value for pH 8.00 does not represent a sharp break in the data. A straight line fitted to the first six points has the equation

$$E = -14.104 + 10.1514 \text{ pH}$$

The slope, 10.1514, has a standard deviation of 7.25 (4 degrees of freedom) and so cannot be considered as different from zero. From this point of view there is no evidence of a linear trend in the data and the constant may be assumed not to vary over the range. Yet there is a very evident pronounced trend in the values which cannot be overlooked. This is confirmed by comparing the standard deviation of the individual entries of sets *a* and *b* as computed, first, from the deviations of the averages from the straight line, and then from the differences between the duplicates. These estimates are 40.2 and 7.7 and are so different that it is obvious that the average values depart from the fitted line to a far greater extent than would be expected from the concordance between the duplicate measurements.

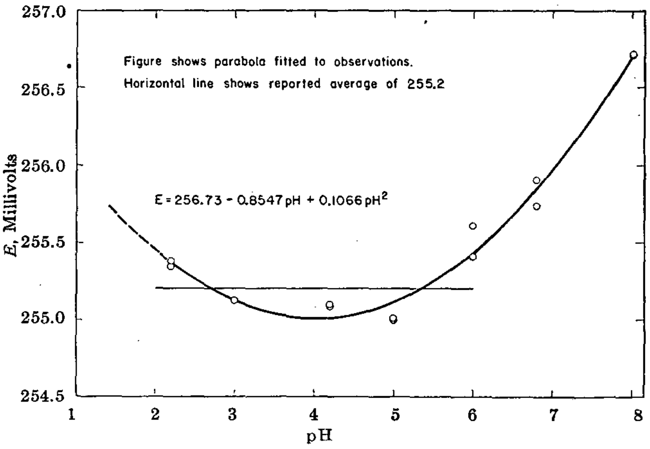

Figure 1

The standard deviation is estimated from the duplicates by squaring the differences between the duplicates and taking the square root of half of the average value of these squares.

$$s_d^2 = \frac{4^2 + 0^2 + 1^2 + 1^2 + 20^2 + 17^2}{2 \times 6} = 58.9$$

$$s_d = 7.7$$

The previously given formula for s^2 is modified by a factor 2 in the numerator, since the observed y is the average of two values.

$$s^2 = \frac{2 \times \text{sum (observed } - \text{ calculated)}^2}{n - 2} = 1619$$

$$s = 40.2$$

Probability tables of a function $F = s^2/s^2_d$ are available (*3*, *7*) to judge the compatibility of the two estimates of the variance (square of the standard deviation).

$$F = \frac{1619}{58.9} = 27.4$$

The table of F is entered with 4 and 6 degrees of freedom and it is found that the probability attached to this ratio is less than 0.001.

The next step is to try fitting the data with a second-degree equation (*2*). This was done, first omitting the values for pH 8.00 and then including this value.

$$\text{pH 8.0 omitted } Y = 172.35 - 85.138 \text{ pH} + 10.6195 \text{ pH}^2$$

$$\text{pH 8.0 included } Y = 172.96 - 85.472 \text{ pH} + 10.6595 \text{ pH}^2$$

The last two columns of Table VI show the values calculated from these two equations. The observed values now agree so closely with the computed values that s estimated from their differences is entirely consistent with s_d computed from the duplicates. This is also evident from an inspection of Figure 1.

The fitting of empirical curves for which no physical interpretation can be made is in general avoided. The empirical curve does serve a purpose in this instance. The literature on the antimony electrode is to the effect that a constant voltage will be found between an antimony and hydrogen electrode in solutions up to pH 8.0. The constant is reported to change at pH 8.0. Yet using data up to only pH 6.80 it has been possible to fit an empirical curve which predicts in an astonishing manner the value found at pH 8.00. The observed value is 171.5 and the predicted 170.9. It is an almost inevitable conclusion that the precision of this piece of work has revealed a real departure from linearity over the whole range of pH. For all practical purposes such as measuring the pH of a solution to 0.01 pH, the deviations are unimportant. From the viewpoint of investigating the behavior of this electrode, the statistical examination prompts a number of remarks.

The equation predicts a value of 74.2 for pH 1.40. If this value were found there would be no question about the general form of the curve. The constant is at a minimum for pH 4.01. It would be extremely interesting to ascertain whether this minimum is associated with the electrode or the buffer solution, by trying some other buffer. The measurements were made at 25° C. and it would not be difficult to determine whether the location of the minimum is independent of the temperature. There is a question here for the mathematical statisticians: Based upon these data, what are the confidence limits for the location of this minimum on the pH scale?

All the above examples make use of the same basic technique of fitting a straight line by least squares and computing standard deviations for the constants in the linear equation. The essential advantage in this technique is the use that is made of the sample weights, the known compositions, or pH values as correlated information. Far too often attention is directed only to the actual observations.

In the last example the several values obtained for the voltage could be replaced by an average and a standard deviation computed from the individual values. By making use of the associated pH variable additional information was obtained. The examples have been chosen to exemplify various possible situations which may be encountered. The actual number of measurements ranged from ten to twenty for all the lines fitted and yet these limited numbers were sufficient to carry the interpretation of the data beyond that found in the published reports from which the data were taken.

Apart from the normal errors of manipulation, observations are subject to various errors that may be inherent in the chemical procedure. These errors may be of the so-called constant type, such as the error arising through impure reagents or a displaced end point in a titration. These are often combated by running a blank on the reagents. If the range of samples taken permits fitting a straight line, a constant error, if present, will be revealed by making use of the slope of the line. If the error is directly proportional to the magnitude of the sample, it will not be revealed by this technique. If the error varies in some manner not proportional to the size of the sample, it may be possible to demonstrate its presence. The work with the antimony electrode is a good example of this. In this case the errors do not arise from deficiencies in the electromotive measurements but result when the electrode potential itself departs from a simple linear relationship. There are cases where such departures are of immense significance. Statistical techniques provide a nice measure as to whether apparent departures need be taken seriously.

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Design of Experiments in Industrial Research

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THIS discussion concerns the place of a relatively unfamiliar technique, design of experiments, in a field which is familiar to most chemists—industrial research.

Academic research is characterized by the ability to refine the experiment in order to emphasize known causes of variability. Unknown, or uninteresting, causes of variability can be removed by improvement of apparatus, isolation of the experiment from disturbing influences, and other methods. This exhaustive elimination of unwanted disturbances enables concentration on the selected topic of interest to the exclusion of all other considerations. Modern industries support a sizable amount of research of an academic nature, but, in addition, they require work in fields in which undesirable sources of variability cannot be eliminated.

These fields of industrial research fall into two classes. On the one hand, industry frequently requires laboratory work with poorly defined tests. Determinations of fatigue life, adhesiveness, resistance to accelerated aging, processability in the factory, etc., are important in numerous fields of industrial research. Tests of this type cannot always be refined to such an extent that the desired differences are clearly distinguishable from experimental error. This inability is, no doubt, a consequence of our imperfect knowledge of the factors underlying such tests but, regardless of its cause, it makes the conclusions of the industrial chemist insecure and troubles him about the best way of setting up his experiments.

Another field of industrial research is occupied by factory-scale or pilot-plant experiments. An attempt to refine these experiments might result in eliminating the most interesting and important features of the problems. Vagaries of operating personnel must sometimes be included, in order to make the final conclusions realistic. Even though the measurements to be made on the final product may be entirely precise, complications of interpretation are tremendously multiplied in going from the test tube to the factory.

These features of industrial research are just those which require careful design of experiments. For many years chemists have been inclined to look down their collective nose at the biologist and the agriculturist. Since research in these lines is particularly aggravated by the type of difficulty described above, biologists and agriculturists have become accustomed to the use of new methods in planning their experiments. These methods, for the most part, were originated by the British mathematician, R. A. Fisher, and his co-workers. The chemist is now in a position where he must venture beyond the safe fields of refined experiment and enter upon problems that demand the utmost skill in designing and interpreting the appropriate experiments. Under these circumstances, it is best for him to swallow his pride and to look for guidance in his present difficulties to fields in which these methods have been proved.

Table I. Block Experiment

	Litter 1	2	3
Pup I	A	A	A
Pup II	B	B	B
Pup III	C	C	C
Pup IV	D	D	D

What is meant by the "design of experiments"? Simply the planning of a group of experiments so that their combined result will yield a maximum amount of information for the work which has been expended. It is important that this planning take place before the experiments are carried out. In addition, it is necessary to consider the analysis which will be applied to the data after they have been obtained, so that there is reasonable certainty of drawing valid conclusions.

A number of standard designs have been invented, one or more of which are capable of handling almost any problem.

BLOCK EXPERIMENT

The simplest type of experimental design is called the "block experiment." Its object is to eliminate, as far as possible, variability of the experimental medium. For example, in rubber technology it is well recognized that the physical properties of a test piece depend on the detailed procedure by which the test piece was mixed and cured. In order to obtain as great uniformity as possible, it has been customary to specify that comparisons be made only among test pieces mixed by the same man on the same day. This is a very rough and inefficient way of eliminating variability of the experimental medium. The problem is more efficiently handled if it is recognized that items of the experiment can be arranged in groups, either in space or in time, so that the variation of the medium will be small within the groups in comparison with the variation expected between groups. (In agriculture, these groups are called blocks. This is the origin of the name of this type of experiment.)

Suppose a nutrition chemist is attempting to compound a ratio for a particular breed of dog, and wants to determine which of four experimental formulas will best nourish growing pups. Differences in rate of growth due to heredity may be as large as or larger than differences due to diet. It is, however, generally admitted that pups from a single litter will be more uniform than pups in general. The block experiment takes advantage of this proposition, at the same time recognizing that the number of puppies in a litter is not great enough to allow for all the desired replications within a single litter. The experiment would therefore be set up as follows: three litters of four pups each are taken for the experiment; diet A is fed to one pup of each litter; diet B to one pup of each litter, etc. This is expressed symbolically in Table I.

The experimenter records weight at a definite age, rate of increase in weight, or some other suitable measurement of the effectiveness of each diet for each experimental animal. The important feature of the experiment is that each diet is represented in each litter. Because of this, the variation between litters can be allowed for in analyzing the experimental results, with a very material increase in accuracy of the experiment. A further advantage of this type of experiment is that the results are more general, since they have been obtained from a more representative sample of the experimental medium than if, in this illustration, it had been possible to obtain the whole experiment from a single litter.

In general, the block experiment is advisable wherever some feature of the experiment is unique in the sense that it cannot be repeated identically in subsequent experiments. It is not always desirable to set up experiments with the amount of repetition shown in Table I. This objection can be avoided by more sophisticated types of design.

FACTORIAL EXPERIMENT

Of even greater general utility than the block experiment is the design known as the "factorial experiment." This design is generally applicable to any experiment where we wish to observe the effects of more than one independent variable. Briefly, it involves selecting a number of independent variables to be studied and the number of values to be assigned to each of these variables, and carrying out a complete experiment for each combination of the different values of all the variables.

For example, the yield of a certain chemical is to be studied in the pilot plant. Preliminary experiments on a laboratory scale have shown that best results will be obtained when the reaction mixture is diluted with approximately 50% of an inert solvent, when the temperature is maintained at 50° or 60° C., and, further, that either catalyst A or B will give substantial amounts of the desired chemical. If the reaction time is rather long, the investigator will wish to begin his search for optimum conditions with a relatively small number of combinations. Suppose he plans to investigate three concentrations of the inert solvent, say, 40, 50, and 60%, and only two temperatures, 50° and 60° C. In addition, he wishes to compare catalyst A with catalyst B.

Elementary science courses teach uniformly that the scientific method involves holding all variables but one constant, and allowing that variable to take a number of values. The observed results will then teach us the effect of that variable. If the investigator has been trained in this school of thought, he may decide to vary the concentration of the inert solvent at a single temperature and with a single catalyst. On completing these three experiments he will pick the optimum concentration of inert solvent and study first the effect of high temperature, and then (at a single temperature) the effect of catalyst B. He might obtain the results shown in Table II.

Table II. Yield of Chemical

		Concentration of Inert Solvent 40%	50%	60%
	Temperature ° C.	Yields *Lb.*	*Lb.*	*Lb.*
Catalyst A	50	45.1	45.7	44.9
	60	...	45.8	...
Catalyst B	50	...	45.7	...
	60	...	...	...

It is fair to assume that the investigator is experienced in this type of experiment. He knows that there is an error of 0.1 or 0.2 pound in weighing the product, and so places little confidence in the third digit recorded in the figures in the table. As a consequence of his five experiments, he will probably conclude that the yields are all substantially the same, so that it makes little difference what are the actual operating conditions of the process within the range here covered.

This is a very unsafe conclusion to draw from the meager data shown. This type of experiment calls for the factorial design. In this case, use of the factorial design means that experiments would have been carried out so as to fill in all of the blanks shown in the table. It is entirely possible that the results might be as shown in Table III.

Table III. Factorial Experiment

	Temperature	Concentration of Inert Solvent		
		40%	50%	60%
		Yields		
	° *C.*	*Lb.*	*Lb.*	*Lb.*
Catalyst A	50	45.1	45.7	44.9
	60	44.8	45.8	44.7
Catalyst B	50	33.0	45.7	53.8
	60	32.6	45.5	54.2

It is at once apparent that, although the amount of inert solvent is unimportant when catalyst A is used, this factor becomes extremely important when catalyst B is used. Results of this experiment clearly indicate the necessity for further investigation before specifying optimum operating conditions.

Admittedly, the data of Table III are fictitious and have been chosen to illustrate the importance of a complete investigation. It is not infrequent, however, in actual experimental work to obtain unexpected results of just this type. A major advantage of the factorial experiment is that it is our best safeguard against missing important information.

A further feature of the data given above must be emphasized. It will be noticed that the effect of temperature is insignificant. The uniformity of results obtained at the two temperatures gives us confidence in the reliability of the data. More than this, however, this design allows an estimate of the reliability of the conclusions without carrying out any duplicate experiments, regardless of the presence of an effect due to temperature. Wherever experimentation is costly, this feature is of extremely great value.

A further point should be noticed. In comparing the effect of high temperature with that of low, the average of the six figures obtained at 60° C. should be compared with the average of the six figures obtained at 50° C. This gives great accuracy to our final conclusions. This method of analysis is justified by the symmetry of the factorial design. To a first approximation, the effects of concentration of inert solvent and the nature of the catalyst cancel out in this comparison. Similar statements can be made for each of the variables involved in the factorial experiment. In consequence, the total information yielded by the factorial experiment per unit of the experiment is very much greater than in any other design.

ANALYSIS OF VARIANCE

In describing these experiments the fact that detailed analysis of the results is contemplated has been mentioned. This analysis is rather more elaborate than that ordinarily used. Techniques are available for separating the total variability exhibited by a set of data into items associated with each of the sources of the variability. In addition, an analysis of this type furnishes an estimate of the error in the experiment and consequently allows a statistical test of the significance of the conclusions. This type of analysis is called an analysis of variance.

A complication arises in many applications of this analysis, whose avoidance requires considerable experience with the experimental medium. In order that the error estimate be valid, it must include all pertinent sources of error; otherwise, the replication is incomplete and serious mistakes can be made.

This situation is most readily explained by a simple illustration. In the outline of the block experiment, it was pointed out that appreciable errors are involved in mixing the recipes from which rubber test pieces are cured. This fact is not always recognized with sufficient clarity in drawing conclusions from experimental data. Suppose an investigator is studying tensile strength of a rubber vulcanizate as affected by three different accelerators Preliminary experiments have shown him the proper quantity of each accelerator to use. He then makes one mix of each accelerator and, according to customary practice, obtains a range of cures from each mix. The tensile data might look somewhat as shown in Table IV.

By inspection, it can be seen that the differences are not large, but it appears that accelerator B gives a higher tensile than does C and perhaps also has some advantage over A.

This conclusion may well be fallacious. All the cures containing accelerator B were made from a single mix. If any mistakes were made in the preparation of the mix, they may affect all the data obtained from that mix. The apparent replication of this experiment is incomplete, in that any errors due top reparation of the original mix are not replicated. There is no doubt but that the tensile strength of the compound containing accelerator B is greater than that containing accelerator A, but it has not been proved that this difference is due to the difference in accelerator.

Table IV. Tensile Data

Cure at 140° C.	Accelerators		
	A	B	C
	Tensile Strength, Lb./Sq. Inch		
Min.			
40	3900	4300	3700
60	4100	4200	3900
80	4000	4300	3600

Under these circumstances definite conclusions can only be drawn when the mixes are replicated. The appropriate design is shown in Table V. This extended experiment shows that in fact there is no difference between the accelerators.

These data are fictitious and correspond to a very poor level of control on the mixing procedure. There are, however, many cases of practical importance where incomplete replication can have very serious consequences.

Table V. Variance Analysis

Cure at 140° C.	Accelerators					
	A	A	B	B	C	C
	Tensile Strength, Lb./Sq. Inch					
Min.						
40	3900	3600	4300	3700	3700	4100
60	4100	3500	4200	3900	3900	4000
80	4000	3800	4300	3600	3600	3800

It will be noted in Table V that the amount of replication given to answering the question, "Is there any difference between these accelerators?" differs from the amount given to the question, "How does tensile strength depend upon cure?" Under these circumstances, a special type of variance analysis is required in which different error estimates are used, appropriate to the amount of replication given to each question.

CONCLUSIONS

An attempt has been made to describe what can be done by the design of experiments, and also some of the circumstances under which experimental design becomes important. Only a few of the features of this subject have been covered A number of other tools are available and have been found to be of extreme utility. The subject is a large one, but its study is rewarding.

Whenever all the information contained in a set of data must be extracted, or whenever results must be obtained as efficiently as possible, the design of experiments can be counted on to bring real benefits to industrial research.

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Statistical Training for Industry

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DURING the past twenty years there has developed a field of activity in industry which has come to be known as statistical quality control. This movement constitutes the introduction of modern statistical methodology into industry, and any discussion of the use of statistical methods in industry or of training in the use of these methods would be incomplete without some reference to statistical quality control and its growth.

Industry has recognized two main aspects of quality control: (1) process control and (2) sampling inspection.

Process control is concerned with the control of the quality of product as it passes through the various stages of the manufacturing process. The control procedures are based on careful statistical analysis of sequences of measurements of quality characteristics made on samples of the product at certain stages in the manufacturing process. When appropriate statistical analysis is used, these sequences of measurements are capable of yielding information promptly as to whether the manufacturing process at a given stage is proceeding at an established state or level of control. The analysis is based on the statistical theory of when the variability, or secular trends, or other types of fluctuations in sequences of measurements become large enough to indicate the presence of causes of important disturbances in the manufacturing process at that stage. This analysis has been highly standardized for routine application in forms known as Shewhart (*1, 7, 8*) control charts.

Sampling inspection is concerned primarily with the control of quality of the completed product by inspection of samples from lots of the finished product, or of samples from lots of finished components of the product. If sampling inspection is nondestructive, so that defective pieces in a lot can be recognized and replaced by nondefective ones, then sampling inspection can be used as a device for controlling the percentage of defectives accepted in the long run. Three general types of sampling inspection schemes have been developed: single, double, and sequential sampling. Any given sampling plan has an operating characteristic curve, which indicates the probability of accepting a lot with any given percentage of defectives. Single and double sampling inspection tables for routine application under a wide variety of conditions have been made available by Dodge and Romig (*5*). The Material Inspection Service of the Navy (*6*) and the Columbia University Statistical Research Group (*4*) have issued sampling inspection tables for all three methods.

Of these two aspects of quality control, process control is the more fundamental in the sense that process control properly established at various stages of the manufacturing process essentially guarantees that the end product will be satisfactory and will, in general, pass any appropriate sampling inspection plan. Sampling inspection as customarily practiced is used by a purchaser to control the quality of the products he buys, or, more specifically, control the number of defectives he will tolerate.

GROWTH OF QUALITY CONTROL DURING THE WAR

Until the beginning of the war only a few scattered companies, mainly in the electrical industry, had become interested in the use of statistical quality control procedures. But a great outburst of enthusiasm for the procedures developed during the war. The reason is to be found in the fact that with the huge requirements of war material, thousands of manufacturers were faced with the necessity of making new and different products in great quantities as rapidly as possible. Army and Navy procurement agencies set up acceptance sampling procedures for deciding whether to accept or reject lots of material. Some manufacturers found that large percentages of their output would not meet these acceptance sampling requirements; they simply needed to improve the quality of their products. Many of them turned to statistical quality control procedures and found them immediately effective in establishing and maintaining control of manufacturing processes.

British manufacturers, operating under heavy war production schedules before the United States had seriously started its war production, came to a fairly general recognition of the value of statistical quality control methods about two years before American manufacturers did. The foremost problem which had arisen in England's wartime quality control experience was that of developing personnel who could introduce and operate statistical quality control methods in industry. The number of individuals who knew anything about the subject in England before the war was totally inadequate to meet wartime demands. The solution decided upon in England was to set up a group of experts in the Ministry of Supply who would be on call by war plants to visit such plants for varying lengths of time and install the procedures—giving enough instruction to personnel on the spot to keep the work going.

By making a study of the wartime development of the quality control situation in England up until the latter part of 1942, the Committee on Applied Mathematical Statistics of the National Research Council anticipated that there would be a similar development with a more serious personnel problem in the United States, with about a two-year lag. It was concluded that the only feasible way to deal with the personnel problem in the United States was by means of a program of short intensive courses in quality control procedures in war production centers throughout the country, which would provide enough training in the rudiments of statistical methods to enable those taking the courses to install quality control procedures in the simpler and most troublesome spots in the manufacturing process in a given plant. Accordingly, a proposal was submitted to the Office of Production Research and Development (OPRD) of the War Production Board, early in 1943, that it sponsor a nation-wide program of short intensive courses of this type. The proposal was accepted and a plan was worked out whereby the courses were administered by the Engineering, Management, and War Training Program of the United States Office of Education through various universities over the country under the general supervision of OPRD. Under this program, 34 short intensive quality control courses were given in approximately 25 cities throughout the country to a total of nearly 2000 individuals representing some 800 industrial organizations.

It is obviously impossible to produce a quality control expert in an 8-day course. All that could be hoped for was to stimulate the individuals taking the course to begin thinking statistically about some of their problems and to show them how to use some of the control chart techniques and acceptance sampling plans on a few simple production problems. The fact that the individuals who took these courses organized themselves into more than twenty local groups throughout the country for the purpose of meeting regularly to discuss new problems and applications of quality control procedures is evidence of a strong continuing interest which these persons have found in the statistical approach to their problems. Early in 1946 these groups, with a total membership of about 1600, organized themselves into the American Society for Quality Control, with headquarters at 305 East 43rd St., New York 17, N. Y.

At the present time, there is wide acceptance of statistical quality control methods in industry. It is not necessary to describe here the ways in which these methods contribute to the efficiency of modern mass production technology. Many articles have been written to show how the methods have been applied to control problems in the chemical industry and dozens of other industries.

OTHER FIELDS OF INDUSTRIAL STATISTICS

The introduction of what are now commonly called statistical quality control methods marks only the beginning of the use of modern statistical methods in industry. The methods which have been introduced and widely used thus far deal primarily with problems of inspection and process control. Highly standardized statistical procedures—control charts and inspection sampling plans—exist for a majority of these problems. A large number of persons in industry know something about these procedures. Further dissemination of information about the methods is being carried forward by such groups as the American Society for Quality Control.

There are many categories in the over-all industrial process in which statistical problems exist and have hardly been touched. By the over-all industrial process we mean the process which begins with raw materials, research, and development and extends all the way through to sales and the analysis of consumer reaction. It is only by showing some concern now about these other large fields of potential application of statistical methods that we can hope to see an orderly development in these fields—as contrasted to the rather hectic development of statistical quality control work during the war.

Industrial Research and Development. One of the most promising phases of the industrial process for the early introduction of modern statistical methods is research and development. In fact, considerable use of statistical methods is already being made on the analysis of properties of materials, of comparisons of experimental methods or processes, of repeated tests of apparatus, and so on. One of the most important considerations in research and development is what has come to be called in statistical parlance the design of experiments. For example, an experiment may consist merely of the comparison of some physical characteristic of a substance treated by processes A and B. If so, how many times should the experiment be performed for each of the two processes in order to conclude with a specified degree of confidence that one process is definitely better than the other? A physical or chemical characteristic of a substance usually depends on several important factors—for example, tensile strength of polymer fibers of a standard size depends on temperature of processing, pressure of processing, source of raw material, and other factors. How should one design an experiment most efficiently in order to determine what combination of values or levels of the factors yields polymer fibers with the greatest tensile strength? How many combinations of different values of the factors should be considered? How many trials should be made for each combination? How should the final set of data be analyzed? What conclusions is one entitled to draw from the results of the analysis? These all depend on statistical considerations in conjunction with technical subject matter, content, and background. Statistical analysis appropriate to such experimental designs is known as the analysis of variance. Statistical problems of this type have been thoroughly studied and the methods tested in several branches of biological science. Some applications are being made in industrial research, but the possibilities here have only been touched.

Other statistical methods can be expected to be useful in industrial research and development. The statistical theory of runs, sequential analysis, order statistics, and multivariate statistical methods should be mentioned particularly.

Design and Specifications. Another important phase of the over-all industrial process where statistical methods are becoming more useful is that of design and specification. If specifications are to be set up in terms of a satisfactory level of performance of a product or a piece of apparatus, they should be set on the basis of the statistical data of satisfactory performance. It is only in this way that tolerance limits for specifications can be set in an efficient and scientific manner. If specifications are prescribed without due regard to the statistical nature of the performance of the product, they may be badly out of tune as far as satisfactory performance of the product is concerned.

Consumer Research. In research and development work on ultimate consumer products such as automobiles, electrical appliances, food, and clothing, there are abundant opportunities to utilize important information which can be supplied only by a sample of consumers, or potential consumers, themselves. Sample surveys of potential consumers are already being used (*2*) to provide information on the size and characteristics of the market or potential market for a given product. After a product has been designed, developed, tested, manufactured, inspected, and sold to consumers, samples of these same consumers are capable of furnishing valuable information to the manufacturer on the performance of his product and how to improve its performance. Consumer research of this type is unquestionably a very fertile field where the manufacturer should concentrate more of his attention in the future. For it is only by consumer research that he is able to keep in close touch with the users of his product and to know at all times how his product is being received and what to do to improve its position. To get reliable information about the product from the consumer requires the application of careful sampling, interviewing, measuring and recording techniques, and appropriate statistical analysis of the results. Work of this type is already being done, but the great bulk of the applications are yet to come.

OPERATIONS RESEARCH IN INDUSTRY

During the war there was an activity known as operations research which seems to have peacetime possibilities that ought to be mentioned in any discussion of statistical training for industry. During the war, British and American groups of scientific personnel were organized and assigned to Army and Navy commands in various theaters of operation for the purpose of making analyses of the performance of men, equipment, and tactics under combat conditions. These groups consisted mainly of actuaries, biologists, chemists, engineers, mathematicians, physicists, psychologists, and statisticians. The groups carried out hundreds of analyses on the basis of data collected in the course of military operations. They presented the results of the analyses and made recommendations to the commanding officers and members of their staffs. As a result of actions based on this activity many improvements were made in the training of men, in the design of equipment, and in the tactical employment of men and equipment. The fundamental tools in all these studies were mathematical and statistical analysis.

There were other types of wartime activity analogous to operations research but not carried out in theaters of operation. The work done by the Quality Control Sections of the Bureau of Ships and the Bureau of Ordnance in the Navy and similar groups for the Ordnance Department and Signal Corps of the Army deserve particular mention. The work performed by these groups is essentially operations research applied to inspection, testing, preparation of specifications, and other problems of procurement of material. Peacetime successors of many of these operations research groups are being continued.

Within a few years, we can expect to see industrial operations research groups attached to the managements of large industrial corporations carrying out analyses of operations analogous to those done by military operations research groups for their commands. The domain of operation for such a group would consist of the various segments of the over-all industrial process mentioned above. They would analyze the performance of men, machines, and processes under operational conditions. Too often these problems appear to have been handled by guesses and hunches. In a period in which there has been plenty of margin to spare, it has been safe to handle such problems on this basis. But these margins are being steadily trimmed and sooner or later these problems will have to be subjected to closer and more systematic analysis.

A statement made by General H. H. Arnold in June 1946, before a meeting of the Institute of Aeronautical Sciences, giving his views on the importance of operational research, applies as well to industrial operations research as to military operations research:

> Rare was the scientist whose interests led him to consideration of what I may call diffuse problems, connected with operational research. The number of scientists and technologists who applied themselves to the solution of the difficult problems associated with operations was pitifully small. I suspect this failure is a reflection upon our method of training. It seems to me we must do something to encourage greater interest in the application of the method of reasoning to the evaluation of problems which deal not alone with machines, but with the integrated combination of men and machines.

NEED FOR BASIC STATISTICAL TRAINING IN INDUSTRY

The greatest obstacle standing in the way of a wider introduction of modern statistical methods into industry at the present time is the lack of trained personnel and training facilities. Of the research personnel now in industry who are concerned with the applications of statistical methods, virtually none received any statistical training in college. They have picked up what they know of the subject through short courses, reading, and discussion. This lack of training is due largely to the very rapid growth in the use of statistical methods in recent years. It is clear from the 20-year history of statistical quality control that it took a war to bring the movement to a stage resembling maturity. It is unfortunate that the methods were not introduced into industry gradually over a longer period of time, so that there would have been an opportunity for the proper development of highly qualified personnel to put them into effect and to operate them accordingly. The colleges and universities of the country have been caught unprepared to provide the type of training required for this work. It will take a number of years for them to evolve a curriculum which will effectively provide the required training. The statistical problems which the future scientist or engineer will encounter will cut across traditional lines. Therefore, in order that he may be properly equipped to deal with these problems, he should have a fairly broad statistical training. The training should cover not only statistical quality control methods as the term is now understood, but the design of experiments, analysis of variance, and many other topics. It should be built into the training of scientists and engineers, as calculus is now made a part of their basic education. This means that a basic course in probability and statistics has to be inserted into an already crowded curriculum. The problem is further complicated by the fact that very few professors are at present qualified to teach such a course.

IMMEDIATE NEEDS FOR TRAINING IN INDUSTRIAL STATISTICS

Until the colleges and universities have had time to adjust their curricula to provide some statistical training for future scientists and engineers, some arrangement must be made for the statistical training of personnel already in industry. Probably the most effective way to begin providing this training is for the few colleges and universities which now have qualified teachers to take the initiative and arrange courses or conferences on various topics in industrial statistics for men of industry in their own localities. This was done in statistical quality control during the war. There is now an opportunity to do a somewhat more thorough and leisurely job of teaching statistics. Recently, a series of eleven 5-hour conferences on acceptance sampling was sponsored by the Newark College of Engineering. This is an excellent example of the type of series of conferences which might be conducted in industrial centers all over the country. The material developed from this series of conferences will be extremely useful not only for similar conferences in other parts of the country, but also for regular college courses in industrial statistics which schools may wish to establish. Other topics in statistical methodology which have wide applicability in industry may soon be ripe for conferences of this type. Analysis of variance and design of experiments are fields which should be particularly useful for chemists.

One of the best methods for introducing new statistical methods into a given field in industry is through sessions like the present symposium, but there must be follow-up meetings for further discussion of the methods in order to be most effective. The local chapters of the American Society for Quality Control, whose members include many research chemists and chemical engineers, are doing excellent work of this kind in the field of inspection and process control. Other chemists in the areas served by these groups, who are particularly interested in process control problems, should find the work of these chapters of interest.

But there ought to be facilities for training in the analysis of variance and design of experiments and eventually in other statistical methods which will be useful in chemical research, development, and production. One effective way to provide such training might be for certain universities to set up full-time summer conferences or short courses of two or three weeks' duration which could be attended by relatively small numbers of chemists. Two kinds of instruction should be given: basic statistical instruction on the methods, together with simple exercises, and lectures on applications by chemists who have been applying the methods in their own laboratories and plants. Such sessions should be informal and interspersed with plenty of discussion. Although there is a great deal of literature on all these methods (much of it in rather mathematical form), this method of learning something about statistical methods would be considerably more effective for men in industry than trying to read the literature individually. Out of the material presented at such conferences it ought to be possible to prepare pamphlets especially for industrial research workers and engineers, similar to those which have been prepared by the American Standards Association (*1*) and the British Ministry of Supply (*3*).

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[Discussions of statistical papers follow on next pages]

Discussion of Symposium Papers

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IN opening the discussion, I should like to make a strong point of the unity of these problems, with each other and with the other problems to which statistics may be applied. In order to do this I shall have to give a definition of statistics, which will make it clear that I do not have in mind what that word meant fifty years ago, merely the organized collection and classification of data. "Statistics is the science, the philosophy, the art, and the technique of making inferences from the particular to the general." The essential element is the element of inference.

If we consider Mr. Smith's economic examples first, we find that the essential part of economic forecasting is the inference that certain changes in economic indexes are likely to be followed, after a suitable time interval, by certain economic results. This inference from particular years past to a general year ahead, is the central point. The use of the inference to predict what will happen "next year" is an application!

In his discussion of the application of statistics to the breakdown of sales data, Mr. Smith approached a place in which economic analysis has not become fully developed statistically. If a thorough job of inference were to be done on this problem we would attempt to assign suitable fractions of the observed differences between areas and salesmen to such effects as the intensity of competition, the levels of business activity and income in the areas concerned, the effectiveness of different sorts of advertising campaigns, and the ability and activity of the individual salesmen. I do not say that I know how to make such an analysis, but I am sure that such an analysis can be made, that the necessary methods can be found.

I should like to disagree gently with some of Mr. Smallwood's statements. I do not think that I can completely agree with this statement: "Academic research is characterized by the ability to refine the experiments in order to emphasize known sources of variability." I think that from the chemist's point of view, astronomy represents as academic a field of research as any among the natural sciences, yet it is very difficult for the astronomer to refine his experiments in order to estimate known causes of variability. There are certain stars there, and it is difficult to get much nearer to them.

To come to a more chemical example, let us consider the discovery of helium, and by that I mean the crucial stage of its discovery. This was not its isolation in modern concentration, or even in the pure state, but rather the early experiments of Rayleigh, who had the idea of preparing samples of "nitrogen" from various sources and determining their atomic weight very precisely. In this experiment he found differences between samples of a magnitude fairly detectable in comparison with his experimental error. At the time, there was considerable doubt in the minds of other chemists and physicists that this difference was really there, since they believed all nitrogen had the same atomic weight. However, this academic experiment, in which the variability of chemical analysis was almost large enough to mask the effects investigated, was the critical thing in adding a new element to those isolated on earth. It was not the later isolation of helium in large quantities, but rather this first inference from data subject to error, and subject to error in substantial amount, that was crucial!

The critical stage in any experimental subject is the stage at which inferences are made, whether they be in industrial chemistry, research chemistry, or astronomy. The difference is in the ways in which these inferences are compared. If the inferences are made during pilot-plant tests the confirmation will come by running the whole process at full plant scale, and finding out whether or not it is economically sound. If the work is in so-called "pure" science, the inference will be confirmed by designing an experiment where the desired effect appears as free from other factors as possible. An example of this last would be the eventual isolation of helium. There is no essential difference in the problems; the apparent differences are inessential—the critical stage is always the inference!

There have always been some people who argue that it is best to avoid statistics if it can possibly be done—many of these are among my friends in academic science. In pure science, this policy may often have paid dividends, but it seems worth while to go ahead and inquire "Why?". It leads to spending much time, effort, and often money on the development of new and more precise experimental techniques and instruments, so that measurements may be made with such precision that the fluctuations can, essentially, be neglected. In many cases a smaller investment in running a large group of experiments with the older and cruder equipment might have led to essentially the same conclusions.

It might seem natural to jump to the conclusion that it was unwise to build the new precise equipment and use it to settle the particular question. There are, I have no doubt, many cases where this is true, but there is something of great importance which is overlooked if the argument is left at this point. That is the use of this new, more accurate equipment to tackle problems which require such high precision in order to make even inferences encumbered by variability. The profits that have been obtained by this process have been in the increased possibility of attacking new problems at the new boundary of available precision, rather than in the definitive settling of old problems.

In industry, with limited budgets not only of money but also of trained manpower and time, there are many places where adopting this policy of avoiding statistically based decisions would mean replacing inference, not certain but with known liabilities, by guessing, with all its dangers. Here the "no statistics" policy is surely bad. Further, in some branches of industrial work, as Mr. Smallwood remarks, in order to make a pilot-plant experiment which really reflects what full operation will yield, it is often necessary to allow for the personal reactions and limited skill of the operating personnel.

This, however, does not mean that the values of "unnecessarily precise equipment" are fully absent in industrial work, since research and development in industry have many of the same values and dangers as research in a purely academic science. However, the complex nature of the confirmation which is to be hoped for in many industrial situations makes it almost certain that an efficient and economical way of carrying out the initial work demands that it be done under conditions where statistical analysis is necessary.

DEVELOPMENT OF WORKING ANALYTICAL METHODS

I should like to carry these topics of the unity of statistical problems and the presence of variability in academic research a little further by considering a problem in the development of working analytical methods. It seems to me that one of the most academic topics which directly interests this group is the study and development of new analytical methods. For the information about the example I am going to discuss, I am indebted to John C. Whitwell of Princeton University, who, with his collaborators, was and is carrying out this work for the Textile Research Institute.

The basic problem was the development of adequate, rapid, and convenient analytical methods for moisture in wool, which could be ultimately used during the processing of wool under various textile operations. After some initial experiments Professor Whitwell set up a moderately complicated experiment which was designed to test the accuracy of five or six methods for moisture determination by comparison with standard determinations made by measuring the loss of weight in two types of ovens. After carrying out an experiment of this sort, using wool from a single hank which had been conditioned in a constant humidity room, it seemed advisable to repeat the whole experiment and to do this it was necessary to use wool from a second hank in the same skein. The results obtained for the moisture as measured by the standard methods did not seem to be in good agreement and seemed to show statistically significant fluctuations. When this fact had been learned, there was a problem in interpretation—should the variation in results here be ascribed to the fact that the wool used came from a second hank on the same skein, or should it be ascribed to the fact that the experiment had been conducted on a different day or days. Consideration of this question from a chemical point of view did not seem to lead to a conclusive answer, and so it seemed wise to make a critical experiment to determine whether or not one of these causes was the important one.

In the critical experiment actually performed, a new skein of wool was conditioned, and then divided into eight consecutive sections; these sections were further subdivided, and balanced samples were made up from each. One sample from each section was run on each of eight days, and the results were subjected to statistical analysis. The results of this analysis indicate: (1) that day-to-day variation seems to be by far the most important, (2) that variation from section to section along the skein is of secondary but still substantial importance, and (3) that the difference between the two types of ovens used was second only to the effect of dates. Later experiments, with the ovens in a room at constant humidity, have shown a marked reduction in the day-to-day variability, and have continued to show significant differences between sections and ovens which occurred in the first experiment. The detailed analysis of the first experiment showed that certain minor effects were present, and that, after the major effects were reduced in the later experiments, they were still found to be present. They were then considerably more noticeable and could have been found by less refined analysis which would have been unsuccessful in the first experiment.

One moral is that, in organizing a complex experiment of almost any sort, it is worth while to arrange to do the duplicate measurements on different days. In almost any case where this has been done, it has been found that the effect of days is statistically significant, and it usually has been possible to trace down this effect to its actual cause, and, in the process, to learn more about the mechanism of the process being studied, and about how to make more precise measurements or obtain more precise results. In this case it was the relative humidity. In some other cases that I met during the war, there was a distinct effect due to the behavior of operators on Monday mornings as compared with other times during the week. Often these variations, these day-to-day effects, depend on things which were wholly unsuspected before the carefully designed experiment was set up.

IMPORTANCE OF REPLICATION

As a source of clues about unsuspected effects and as a source of an honest estimate of the variability inherent in the measurements, I can recommend nothing more highly than the replication of analyses, tests, or experiments at different times. As Mr. Smallwood has said, we learned at an early stage in our chemical career to make analyses in duplicate if not triplicate (I think I am entitled to use the word "we" here since I used to be a chemist). The thing that we did not learn was that to get reliable values for the parallel analysis of three unknowns with an honest estimation of the errors of analysis, we would do very well to carry one duplicate of each of the three unknowns through on a single day, and repeat this process on two more days, rather than using the more customary practice of running three duplicates for each unknown on the first day, and then three of each succeeding unknowns on each succeeding day. Many of my academic friends in chemistry and physics and other sciences are among those furthest from realizing the importance of this day-to-day part of experimental design. I see no reason why the chemists in industry and analytical chemists engaged in research should not lead the whole chemical profession into a better understanding of the need for such replication at different times and of the importance and advantages of statistical methods.

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THE application of precise techniques of analyzing data is one of the most difficult problems we face today in modern science. Among those unacquainted with, or unconvinced by, statistical methods, there are apt to be two quite opposing attitudes. Some claim that the data they obtain are far too irregular to be subsumed under the conditions of mathematical formulas. Others claim that their data are so precise that no analysis is necessary, the answer being apparent on inspection. Both points of view miss the critical phase of the problem of application. It is perfectly conceivable to handle very erratic data, provided certain assumptions can be made about their origin. And it is sometimes very wasteful of information to ignore a statistical analysis of very exact data, since with the exactness comes additional information, as Dr. Youden points out.

The critical point about the application of statistical techniques is "What assumptions can be made about the data and the importance of the problem?". This is not a question that the statistician can answer. He can only tell the experimenter what should be done, what inference can be drawn, what design to use what control limits to employ, when he knows that certain assumptions are valid. But the experimenter himself is often at a loss to state his assumptions in a form that is comprehensible to the mathematician.

As an example, let us suppose the chemist is convinced by Dr. Smallwood's very excellent account of the analysis of variance, and decides to try it on his own data. Now it would be a very serious mistake to assume that the statistical method can be applied to any set of data that can be arranged in categories of the kind Dr. Smallwood illustrated. There are certain assumptions, some critical, some not, that must be made in order to assure that the results of the analysis are legitimate. But the decision as to whether the assumptions hold is a matter for the chemist, as well as the mathematician, to decide.

MEETING OF MINDS

This implies that the proper application of statistical techniques demands a "meeting of minds." The mathematician knows what his techniques will do, provided he assumes certain things about the origin of the data. The chemist knows what he is after, and what conditions he has imposed on the data by his laboratory techniques. The job is to get the two speaking the same language, so that the proper cooperation will result. The simplest way of accomplishing this job, of course, is to try to make the chemist into something of a statistician, and it is certainly important that chemists come to know more about statistical methods and their language than they do at present. But many technical difficulties arise in the application of the methods, and to be competent to handle all these matters demands a very thorough knowledge of the field of mathematical statistics. Because of the finite time each of us has to pursue his work, we cannot expect the chemist to become an expert in some other field, no matter how valuable its contributions may be. The alternative answer is to form some kind of basis for cooperative research, some kind of "operations analysis," where a group of scientists act as a team, each contributing something of his own specialty, each learning from the other what must be known in order to arrive at an adequate solution.

This does not mean, of course, that chemists should not try to apply statistical techniques themselves. This would be like saying that no one should take an aspirin without consulting a doctor. But, on the other side, the blind application of statistical methods to all problems, no matter how complex and difficult, is like taking an aspirin to solve every ill. In some cases it is important that patient and doctor cooperate in discovering the solution to a problem.

One other aspect of this problem of a meeting of minds in problems of application is often neglected. When we start to learn about statistical methods, we are always faced with two problems:

1. Where should the level of significance be set?
2. What sample sizes should be used?

Textbooks usually answer the first by some such remark as: "The level of significance is usually set at 0.05, or 0.01, depending on the importance of not rejecting the hypothesis when it is true." And the instructions on sample sizes are equally vague. The reason for all this is that we have no precise techniques for setting significance levels and sample sizes. In general, neither the chemist nor the mathematician can give the required information. These are matters that must be settled by the "consumers" of research. After all, research, industrial control, etc., are as much consumer products as are automobiles, soap, and suits, and it is the consumer who is supposed ultimately to resolve the problem of cost and quality. We can supply research at low cost, with small sample sizes, but the risks will be large. Or we can supply high quality research at high cost. The mathematical statistician, like a product engineer, can design the equipment for either end. The choice is up to the consumer, whoever he may be, the manufacturer, the buyer of goods, the theoretical chemist. What the research is to be used for is what sets the significant levels and sample sizes. And today we are hopelessly behind schedule on this important aspect of science. At the risk of appearing facetious, I would like to extend Mr. Smith's discussion on market research and suggest some considerable attention to the problem of market research on research itself. We need to find out what the consumer of research wants, what risks he is willing to take, what quality of knowledge he is willing to have presented to him.

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PROFESSOR Wilks mentioned the fact that most of the people now using statistical methods to help solve industrial problems have picked up what they know of the subject through short courses, reading, and discussion.

All of us who obtained our training in this way are in complete agreement with Professor Wilks when he suggests that future scientists and engineers should have fairly broad statistical training in the universities, not only in quality control, but also in the design of experiments, analysis of variance, correlation, etc. Until such time as the universities can supply this training, I think his suggestion of short intensive training courses is very workable and I hope it will be followed.

I believe Dr. Youden's method of treating experimental data is new to most chemists. It should find use in those cases where it is difficult to prepare known mixtures for use in studying the reliability of test methods.

For example, it is often very difficult to prepare samples which are like the fermentation mashes encountered in the production of such substances as acetone or some of the alcohols. By the proper use of Dr. Youden's technique much information could be obtained about the precision and accuracy of a test method for, say, acetone in a fermentation mash using samples of production lots of the material. The precision and accuracy of test methods for alloys could also be studied using the alloys themselves. It will always be necessary to make up some known samples when studying a new and untried test procedure but here, too, Dr. Youden's technique should help get the maximum amount of information from the test results.

We should always keep in mind the two important assumptions which are made in using this technique: (1) that the x values have relatively smaller variability than the y values; (2) that the variability of the y values remains about the same up and down the line. Fortunately, from a practical point of view, most experimental data conform to the first assumption and it is only rarely that both the x and the y values are equally reliable.

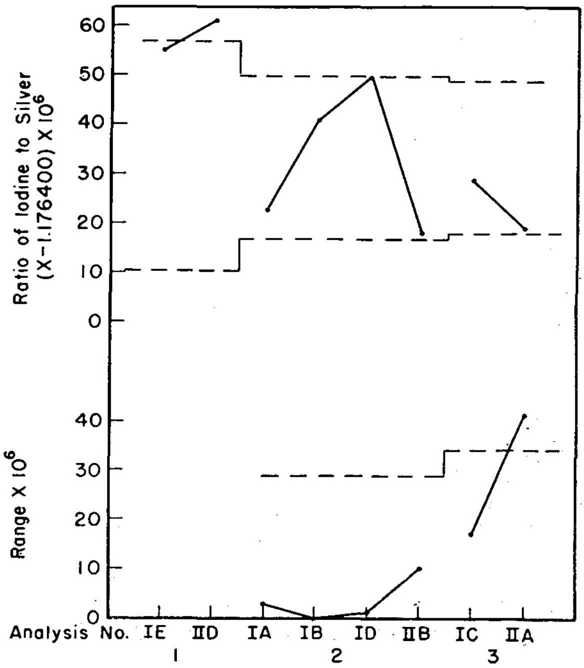

Figure 1. Control Chart for Iodine to Silver Ratios

Data from 11th Report of I.U.C. committee

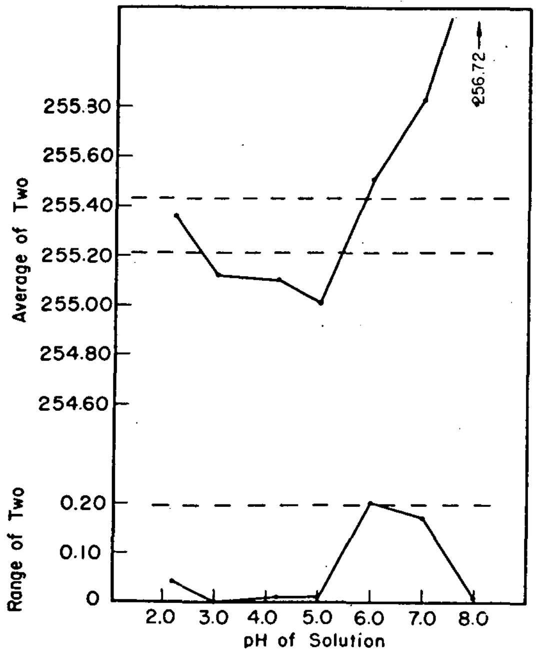

Figure 2. Control Chart for Voltages across Antimony and Hydrogen Electrodes

Data of Hovorka and Chapman

Even when this is the case something might be done to make the x values more reliable. For instance, in the study of the modified Babcock method *vs.* the standard A.O.A.C. method for the determination of fat in meat, the standard A.O.A.C. method might have been replicated several times for each sample of meat and the average values plotted as the x values against individual y values for the proposed method. Experimental data do not always conform to the second assumption and we should always be on the watch for changes in variability caused by a change in sample size or amount of constituent present.

Statistical methods, such as this one, often seem more involved than they really are. Chemists need to know the general principles back of the statistical methods they use, but they surely do not need to be trained mathematical statisticians. We all understand the principle of logarithm tables and yet few of us can demonstrate the mathematics by which the tables are computed. Chemists should learn to put what has been called "operational meaning" behind their statistical calculations. In the final analysis it is this operational meaning that makes statistics valuable to the chemist; the calculations have relatively little to do with it.

CONTROL CHARTS

Chemists might well start to apply statistical methods by the way of control charts. A control chart may be described as a graphic presentation of test data in such a manner that the variability of all the results is compared with the variability within (arbitrary) small groups of the test results. The chart is said to show evidence of "control" when there is no more variation throughout the entire set of results than corresponds statistically to the average variation within the (arbitrary) small groups.

We can get a good idea of how a control chart works in the case of a predictable "controlled" experimental procedure by drawing marked chips from a bowl and plotting control charts of the results. Walter A. Shewhart has published the results of such an experiment ("Economic Control of Quality of Manufactured Product," New York, D. Van Nostrand Co., 1931). Control charts for these drawings along with control charts for several types of Analytical Laboratory test data have also been published [Ind. Eng. Chem., Anal. Ed., **18,** 859 (1946)].

To illustrate the use of simple control charts, I have plotted (Figure 1) the data for the ratios of iodine to silver which Dr. Youden examined by the method of variance analysis.

The lower graph is for the range of replicate determinations made on the same iodine-silver combination. One of the six ranges shows evidence of being more variable than it should be by chance variation alone. The upper graph shows one of the individual values to be out of control, and three of the six averages are near their control limits. It is safe to infer that these results show more variation among the different iodine-silver combinations than exists on the average within the combinations. This is the same inference that one is led to make from the analysis of variance.

A control chart for the antimony electrode e.m.f. data is shown in Figure 2.

The lower graph shows the variation of two readings made at the same pH. One of the values is again near its control limit, which leads us to suspect that the variations of duplicate readings may not be entirely random. The upper graph for averages shows unquestionably that the variation from one pH to another is much greater than corresponds, statistically, to the average variation of e.m.f. values at any given pH. It can also be seen that no straight line could be drawn through the data, so that control limits above and below the line would include all of the averages. These conclusions are similar to the conclusions that Dr. Youden got from the use of variance analysis.

I do not want to suggest that chemists can solve all their statistical problems by the use of control charts. Chemists should be encouraged to learn how to use all the statistical techniques they can. However, chemists may well introduce themselves to the use of statistical techniques by way of the simple control chart.

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DR. Youden's exposition indicates the inadequacy of the opinion unfortunately still widespread among physical scientists, that the statistical method is nothing more than a substitute for more cogent methods in places where the latter cannot be applied. This view overlooks, for example, the theory of errors of measurement and the efficient design of scientific experimentation, both of which can be approached effectively by statistical theory only. Dr. Youden has presented very appropriate examples of both these aspects, examples which I should like to re-examine briefly.

In the study of the antimony electrode, a statistical examination of the errors of measurement led to the discovery of a new causal relationship—namely, the parabolic nature of the dependence of voltage across the electrodes on pH. Now the errors of measurement which, in this example, can certainly not be considered excessive, are nevertheless sufficiently large to obscure this relationship, as shown by the fact that the experimenter himself had failed to discover it. It can be concluded that even for errors of measurement which are of the order of magnitude of the effect under consideration, it is possible to isolate this effect by statistical means, provided the design of the experiment is adequate. In this example the adequacy of the design consists simply in the fact that duplicate measurements were available for every pH value.

In the example cited by Dr. Youden concerning the atomic weight of iodine, it was stated that every statistician will regret the absence of a well-balanced design for the five silver preparations and the two iodine preparations. I can whole-heartedly concur in this assertion, and should like to add this remark: Even if the errors of measurement are appreciably smaller than the differences due to different silver or iodine preparations, the true relationship does not become clear until a balanced design, supplemented by an analysis of variance, brings these differences out in full. As the complexity of the experiment increases as, for example, in the case of more than two reacting substances, this becomes of increasing importance.

METHOD OF LEAST SQUARES

The theoretical background of the fitting procedure used by Dr. Youden is the method of least squares. Consider the linear relation

$$y = \alpha + \beta x \tag{1}$$

where, for example, x is the weight of the sample and y the weight of the precipitate. The basic assumptions for the fitting procedure as used by Dr. Youden are:

1. x is, for all practical purposes, determined with complete accuracy.
2. y, on the other hand, is subject to error. Thus, for a constant value of x, we may find random fluctuations in replicate determinations made on the corresponding y. If we represent the fluctuating part of y by δ, we can write Equation 1 more accurately as follows:

$$y = (\alpha + \beta x) + \delta \tag{2}$$

The variable δ, although it represents merely an error of measurement, is none the less of fundamental importance in deciding how one shall estimate the unknown parameters α and β. In physical terms, δ is characterized by the intrinsic precision with which y is measured, and the best way of evaluating this precision is to calculate the standard deviation of δ.

Most textbooks, in explaining the method of least squares, fail to emphasize this point. They also make the tacit assumption that the standard deviation of δ is the same for all x. The analytical chemist knows, however, that in some cases a larger sample will result in larger absolute variations in the weight of the precipitate, while in other cases the size of the sample will have little effect on these errors. In other words, there will be cases where the standard deviation of δ, σ_δ, is actually independent of x, while in others we may have such a relation as

$$\sigma_\delta = kx$$

where k is a numerical constant.

The usual procedure of least squares for finding values of α and β is based on the assumption that r_6 is constant. What can be done if this assumption does not hold true?

Consider again the case

$$\sigma_\delta = kx$$

Then we have:

$$\sigma_{\delta/x} = k \tag{3}$$

Thus the standard deviation of δ becomes constant, provided every δ is divided by the corresponding x. Now we have:

$$y = (\alpha + \beta x) + \delta$$

Hence:

$$\frac{y}{x} = \left(\alpha \frac{1}{x} + \beta\right) + \frac{\delta}{x}$$

We have thus reduced our case to the classical equation of least squares, since $\sigma_{\delta/x}$ is a constant according to Equation 3. But our independent variable is not x, but rather $1/x$, and our dependent variable is y/x. Moreover, the intercept α is now the slope, while β, the slope, has now become intercept.

In order to simplify the notations, let us denote $1/x$ by u and y/x by z. Then:

$$z = (\beta + \alpha u) + \delta'$$

where δ' is written for $\frac{\delta}{x}$ and satisfies the usual conditions (zero average and constant standard deviation).

The method of least squares can now be applied according to the usual technique, with u as the independent variable and z as the dependent variable. The formulas cited by Dr. Youden for the computation of s^2, s_a^2, s_b^2, t, etc., remain applicable, provided one keeps in mind that s^2 refers to δ'—i.e., $\frac{\delta}{x}$—and that a and b have their meanings interchanged.

For any given x, the variance is found by

$$s_\delta^2 = s_{\delta' x}^2 = x^2 s_{\delta'}^2 = x^2 s^2$$

As an illustration consider the following data given by Williams and Haines [IND. ENG. CHEM., ANAL. ED., **16**, 157 (1944)] in support of a determination of sodium in potassium hydroxide. The authors obtained the following results:

NaOH Added (x) $\% \times 10^{-3}$	NaOH Found (y) $\% \times 10^{-3}$	Error $\% \times 10^{-3}$
0	3	+ 3
0	3	+ 3
2	6	+ 4
10	14	+ 4
50	50	0
100	96	− 4
498	481	− 17
995	922	− 73
1990	1853	−137

From the third column it is apparent that the error is definitely increasing with x, and therefore the least squares method, applied without previous adjustment of the data, is misleading. However, if one omits the first two determinations (the blanks) and takes the error as proportional to x, as in Equation 3,

$$a = \text{intercept} = 4.14 \times 10^{-3}$$

$$b = \text{slope} = 0.937$$

In chemical terms this means that the proposed method of analysis has a blank of $4.14 \times 10^{-3}\%$ and a recovery factor of 93.7%. This blank value was obtained without actual blank determination. The latter gave 3×10^{-3} and it is seen that the agreement is not too bad. Moreover, the value $s^2 = 0.000749$ is obtained for the error of δ'; whence $s = 0.0274$. For $x = 0.083$, this would give $0.083 \times s = 0.0023$. The authors, who made 10 additional determinations for $x = 0.083$, obtained $s = 0.0029$. Again the agreement is rather close.

The adequate choice of the nature of δ, in this case the fact that the standard deviation of δ is proportional to x, leads to a correct evaluation of the blank, without performing blank determinations. It also leads to the estimation of the recovery factor and to an evaluation of the precision of the method, without replicate determinations, and valid over the whole range of x examined.

[End of Symposium on Statistical Methods]

Control of the Accuracy and Precision of Industrial Tests and Analyses

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The analytical test is most important in the successful control of the production process. If the process is to be kept in an optimum state of control, the accuracy and precision of control tests must be ensured. Statistical methods have proved to be a powerful tool in accomplishing this objective. The control chart method can be applied to data obtained from repeated analyses of a check sample and to production control data, and can measure and determine the accuracy, precision, and reliability of a control test. A statistical study of the control tests can determine whether the test is accurate and precise enough for the purpose intended, and whether the method is unreliable—that is, subject to abnormal variations at different times or under different conditions. When used in parallel with actual production tests, the control chart can detect errors in the preparation of solutions and inaccuracy due to changes in temperatures, humidities, or other conditions. The method can also be used to determine agreement between analysts and laboratories. Test methods can be compared and the best for the purpose selected. The control chart procedure and its application are reviewed and several examples of its use in controlling the accuracy and precision of production chemical tests and analyses are presented.

IN THE chemical industry the chemical test or analysis is the guide or compass for the operation of the chemical process. From raw material selection to final product inspection, chemical tests are the controls and checks by which the production process is kept within standard limits and is balanced to obtain optimum results. No manufacturing process will operate at highest performance without continuous control and occasional adjustment. Corrective action in the right place, at the right time, is the key in the situation. In the chemical industry the need for corrective action is generally revealed by the result of a chemical test or analysis (Figure 1).

The chemical test or analysis used in the production process is often one of the weakest steps in the system of process control. Methods for measuring the efficiency of production chemical control tests are not generally understood and methods for controlling their accuracy and precision during production have not been clearly set forth. A number of investigators have presented practical procedures, notably Moran (*5*), and more recently, more refined statistical procedures have been discussed (*3*, *4*). The powerful principles of Shewhart (*6*), which have proved so valuable in quality control, have not been generally used by chemists in controlling the accuracy and precision of chemical tests, undoubtedly because of the special problems of setting up the method for control of a chemical test and interpreting the statistical results in terms of a chemical nature. The procedure, as applied to quality control, has been well described by the American Society for Testing Materials and the American Standards Association (*1*, *2*). The applications of these methods in the analytical laboratory have been covered by Wernimont (*8*). These quality control methods have been found most valuable in controlling the accuracy and precision of chemical tests and analyses in the author's laboratories. They provide an accurate statistical tool for production and laboratory use with a minimum of mathematics. The purpose of this paper is to encourage the use of this method in the control of chemical tests and analyses and to present some details of experience with it. The use of these techniques can improve the control of the production process and, therefore, the quality and efficiency.

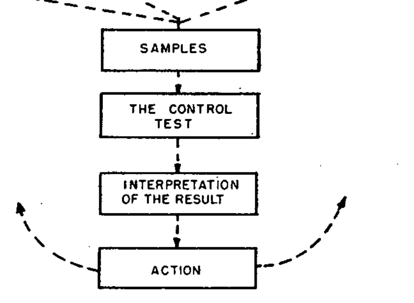


Figure 1. Position of Chemical Control Test in the Chemical Industry

The control of the process is also dependent upon accurate sampling and correct interpretation of the test result. Sampling may be a simple or complex problem, depending on the nature of the product and the process. Interpretation of results is usually the responsibility of the production supervisor and is the attempt to learn the truth about the chemical process from the data available. Not only the present test result but the history of past test results and the correlation of other process information will enter into the step of interpretation. These are separate problems and are not treated here, except from the point of view that errors involved in chemical tests are an important factor in interpretation.

The fact that an industrial plant has a well-equipped laboratory and is using well-designed chemical tests does not of itself ensure correct or reliable test results. Experience has shown that tests in constant use are subject to many unsuspected sources of error. Chemical reagents deteriorate and those from different sources are not uniform, equipment wears and breaks down, and technicians and techniques vary. Unless specific means are used for maintaining the accuracy and reliability of a test method, there is no basis for assuming that results are accurate or reliable. These means include the choice of sound scientific methods, reagents, and equipment and the correct training of analysts and technicians. It is the practice in many laboratories to utilize known standards as check samples at regular intervals. This type of procedure, when followed at regular intervals in a scientific fashion and analyzed by modern statistical methods, is believed to be the most efficient method for controlling the accuracy and precision of a chemical test method.

EVALUATION OF THE CHEMICAL TEST OR ANALYSIS

The chemical test or analysis may be considered a system of causes which will produce a test result from a sample. Normally, a series of unknown samples from production is submitted to the test and the results are used to control the process or product. In order to evaluate the test it is necessary to submit known samples for analysis and to examine the results. This may be most simply done by selecting a known sample of material and submitting to the test identical portions of the sample over a period of time. If the composition of the sample is known, the test results may be used to estimate the accuracy, precision, and reliability of the test. These estimates must, however be used only under the conditions tested. The accuracy, precision, and reliability may vary considerably with the percentage of the chemical being determined, and variations in other impurities may have a similar effect. The effect of these factors cannot be estimated by the study of a single known sample. Many known samples must be studied under the full range of variation obtained in practice, and the use of correlation technique will be found useful in these cases. However, in industrial control work, the range of variations of the chemical samples submitted to test is generally small, because production methods utilize the principle of standardization, and chemical products and intermediate reagents are controlled to remain uniform. Most chemical tests are designed to determine whether chemical materials are within standard or specification.

It is therefore possible to plan a system of check analyses of a given known sample over a period of time, which is applicable to many tests and analyses, especially industrial control test and analyses, and which will measure the success of the test or analysis. The design of a check procedure which will submit constant samples to the analysis, and will check the test under actual production conditions, is vital to success and is a matter of the skill of the analytical chemist in cooperative work with the production engineer. Special precautions and procedures must be used in the case of unstable materials. These identical samples should be submitted in such a manner that they will be analyzed by all analysts working on the actual control tests, using all the equipment, at all times of the day. In any circumstances in which the knowledge of the check sample will influence the analyst's result, it is desirable to submit samples which cannot be distinguished from actual production samples. The check procedure should be established and samples submitted at regular intervals while the test is being used in production. The data should be examined closely and analyzed to measure the success of the test method.

It is a universal observation that when a series of identical known samples is repeatedly tested, the test method will produce results which vary. This variation may be relatively large or may appear only in the last of many decimal places, but will always be present if the results are reported to sufficient figures. The causes of this variation are many and are ultimately traced to the limitations of men, materials, machines, and methods. The variation in the test results is an important characteristic of the test which must be measured. It is because of this variation that statistical methods are necessary in this work. When the results of the repeated analyses of the check material are examined in chronological order as in Figure 2, the characteristics of the test which determine its value may be illustrated.

The amount of variation in the check analysis data is a measure of the precision of the test. This variation is most accurately expressed by the universe standard deviation, σ', which is the standard deviation of an infinite number of check analysis results obtained under the conditions of the test. It cannot be measured directly but can be estimated from the standard deviation of the data obtained. The standard deviation obtained from the data may differ considerably from the universe standard deviation, especially if the number of values obtained is not great. If the standard deviation is determined a number of times from different groups of data, then the universe standard deviation may be estimated from the average standard deviation, $\bar{\sigma}$, by division by c_2, where c_2 is a constant depending upon the number of values in the groups of data. This constant, c_2, corrects the tendency of the observed standard deviation to be too small when the number of determinations is not great.

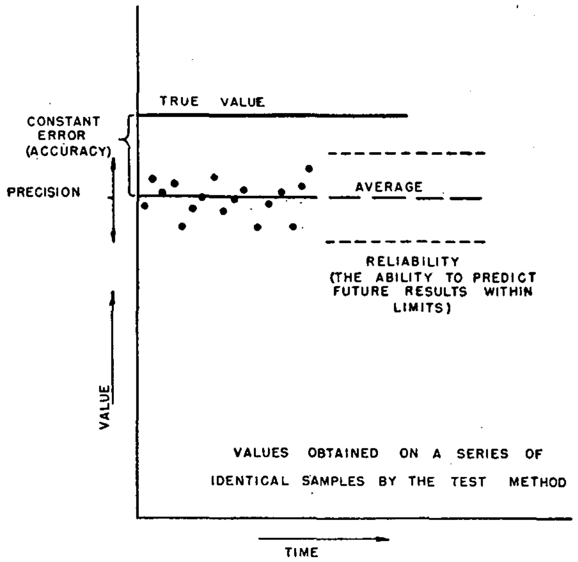


Figure 2. Illustration of Accuracy, Precision, and Reliability of a Chemical Control Test

Precision. Measured by universe standard deviation $= \sigma'$ (1)

$$\text{Universe standard deviation may be estimated from } \frac{\bar{\sigma}}{c_2} \quad (2)$$

An expression of the precision in terms of a standard deviation is not directly interpretable to most analysts and production supervisors. A more useful expression of precision is a range of variation above and below the average which will include practically all check results. No finite range can be expected to include all the values which could be obtained by repeated analyses of the check sample. However, any given range may be expected to include a certain fraction of the values. Practical experience and statistical theory enable us to select a range about the average expressed in terms of the universe standard deviation which will include practically all the data. Such a range is the average ±3 times the universe standard deviation. This range will include 99.7% of a normal distribution of data, but without proving that a normal distribution frequency has been obtained it is better to regard this range as including "practically all" the variation (95% +). This range has significant meaning because of its history of useful value as well as its theoretical derivation. It has proved to be a constructive measure of precision in these laboratories.

Precision. Measured by limits of variation $= \pm 3\,\sigma'$ (3)

$$\text{Limits of variation may be estimated from } \pm 3\,\frac{\bar{\sigma}}{c_2} \quad (4)$$

$$\text{Precision measured by relative limits of variation } = \pm 3\,\frac{\sigma'}{\bar{X}'} \quad (5)$$

Relative limits of variation may be estimated from $\pm 3 \dfrac{\dfrac{\bar{\sigma}}{c_2}}{\bar{\bar{X}}}$ (6)

where X' is the true average result of the universe—that is, the average value if an infinite number of results were obtained. $\bar{\bar{X}}$ is the best estimate of X' and is the average of all X values obtained.

The accuracy of a test or analysis is measured by comparison of the observed values with the "true" value. The methods for measurement of accuracy have been discussed in many papers, but the simplest and most useful concept is one in which the variations of the data are omitted from the measurement of accuracy by comparing the average of the observed values with known true value. In industrial work, the known true value of the check sample is often determined from known chemical composition, more accurate and precise method of analysis, or arbitrary definition. In many cases, no true value can be accurately determined, and a strict interpretation of accuracy is not possible. Arbitrary definition of the true value of the check batch will aid in standardization of the industrial test in this case. Thus an analytical method may have (1) a high degree of accuracy and precision, (2) a high degree of accuracy and a low precision, (3) a low degree of accuracy and a high degree of precision, or (4) a low degree of accuracy and a low degree of precision. If $\mathbf{X}$ is the true value of the sample tested, and X' the true average value obtained by the test method, the constant error or the inaccuracy of the method is:

Accuracy. Measured by constant error $= X' - \mathbf{X}$ (7)

or

Accuracy measured by relative constant error $= \dfrac{X' - \mathbf{X}}{X'}$ (8)

The average from a limited number of values is only an estimate of the true average of the test and we may be able only to estimate the accuracy of the test.

The limits of uncertainty of the observed average of a given number of values may be estimated from the standard deviation and the number of values obtained. If we still use a probability limit corresponding to $3\,\sigma'$, then the limits within which X' may be expected to lie in practically all cases is the following:

$$\text{Estimated limits of } X' = \bar{\bar{X}} \pm 3\,\frac{\sigma'}{\sqrt{N-3}} \qquad (9)$$

where N = total number of values included in $\bar{\bar{X}}$.

If the known or standard value of the check batch falls within these estimated limits of uncertainty the analysis as performed must be judged as accurate, as far as can be determined from the data on hand. If the known value of the check batch is outside these limits, the constant error may be estimated by the following formula:

$$\text{Estimate of constant error} = \bar{\bar{X}} - \mathbf{X} \qquad (10)$$

$$\text{Estimate of relative constant error} = \frac{\bar{\bar{X}} - \mathbf{X}}{\bar{\bar{X}}} \qquad (11)$$

The reliability of a test or analysis is a characteristic of a test which is of major importance in industrial control. The factory man wants assurance that the test method will give him the information which he needs, not just today, but 24 hours a day, tomorrow, and every day of the coming year. It may be understood that the method has certain inherent errors and that the precision is of such a degree that a certain variation will be continually encountered; if the method is reliable—that is, can be depended upon to maintain its present accuracy and precision—the production supervisor can interpret results within the limits of the test and will be prepared to take correct action. If, on the other hand, experience has thrown doubt on the reliability of the test, the production supervisor cannot depend on the results within any reasonable limits; his interpretation is undermined by uncertainty, and his action may be faulty.

This concept of dependability we term the reliability of the test method. The reliability of a test or analysis is the ability to maintain the accuracy and precision of the test into the future with no more variation than may reasonably be attributed to chance. A method is stated to be reliable when we can predict the future accuracy and precision of the method within limits. The reliability of the chemical test, or more specifically, of the test, analysts, equipment, and other components of the test system, can be determined only by checks over a period of time. From a practical point of view, a test will be considered reliable, if in accumulated experience it has always been found reliable. This general concept corresponds with the statistical concept of "state of control," which may be determined by the control chart. If the data show lack of control, the test will be considered unreliable.

The facts which the analytical chemist should understand concerning the state of control are summarized below.

Reliability determined by state of control.

A. When a set of data is obtained from a system such as an analytical method, the data may or may not be in a state of control.

B. The data are tested for state of control by subgrouping them according to time sequence or other logical groupings and determining whether or not there is more variation in the average and standard deviation of each group than can be assigned to chance. This is most easily done by the control chart method, in which control limits are found for the average and the standard deviation of the subgroups. If sufficient numbers of points are all within the control limits, this is an indication of a state of control. If some of the points are outside the limits, this is strong evidence of lack of control.

C. When the data are within control there are cogent reasons for believing that they are from a constant chance system. The chemical test may be judged reliable and its future variation may be reasonably predicted within limits.

D. When the data show lack of control, they are from a system of changing causes. Assignable causes of variation are present and should be sought and eliminated. The chemical test should not be expected to give reliable results.

E. When the data show lack of control, no predictions concerning the average or the standard deviation of the universe can be made. Statements of accuracy or precision will not be dependable and probably will be in disagreement with later tests.

The chemist and production engineer may make quantitative use of these principles by means of tables or factors which have been determined from modern statistical theory. These factors are used in simple formulas to calculate limits within which the estimated average and standard deviation can be related to the true universe average and standard deviation with a given probability. These factors have been calculated for a probability of 0.997 (corresponding to a range of ±3 times the standard deviation) for quality control work and may be applied to control of chemical tests and analyses with the assurance that these limits will include practically all cases when the data are in a state of statistical control. Tables of these factors are available in an A.S.T.M. manual on presentation of data (*1*) and in American Standards Association war standards (*2*) Z1.1 and Z1.3. Nomographs based on some of these factors are also available in Simon's manual (*7*) (Table I).

In industrial control work, the most useful evaluation of a chemical control test has been found to be its reliability, accuracy, and precision, which can be determined in most cases by a study of check sample analyses and a measurement of (1) state of control, (2) average, and (3) universe standard deviation.

Table I. Factors for Computing 3 − Sigma Control Limits

No. of Observations in Sample	Chart for Averages, Factors for Control Limits			Chart for Standard Deviation			Chart for Ranges			No. of Observations in Sample
				Factor for central line	Factors for control limits		Factor for central line	Factors for control limit		
N	A	A_1	A_2	c_2	B_3	B_4	d_2	D_3	D_4	N
2	2.121	3.759	1.880	0.5642	0	3.658	1.128	0	3.268	2
3	1.732	2.394	1.023	0.7236	0	2.692	1.693	0	2.574	3
4	1.500	1.880	0.729	0.7979	0	2.330	2.059	0	2.282	4
5	1.342	1.596	0.577	0.8407	0	2.128	2.326	0	2.114	5
6	1.225	1.410	0.483	0.8686	0.003	1.997	2.534	0	2.004	6
7	1.134	1.277	0.419	0.8882	0.097	1.903	2.704	0.076	1.924	7
8	1.061	1.175	0.373	0.9027	0.169	1.831	2.847	0.136	1.864	8
9	1.000	1.094	0.337	0.9139	0.227	1.774	2.970	0.184	1.816	9
10	0.949	1.028	0.308	0.9227	0.273	1.727	3.078	0.223	1.777	10

Chart for	Formulas	
	Central line	3 − Sigma control limits
Averages	$\bar{\bar{X}}$	$\bar{\bar{X}} \pm A_1\bar{\sigma}$, or $\bar{X}' \pm A\sigma'$
		$\bar{\bar{X}} \pm A_2\bar{R}$
Standard deviations	$\bar{\sigma}$	$B_3\bar{\sigma}$ and $B_4\bar{\sigma}$
Ranges	$\bar{R}$	$D_3\bar{R}$ and $D_4\bar{R}$

This table is prepared from Table I, page 50, Supplement B, of (*1*) and is reproduced through the courtesy of the American Society for Testing Materials.

CONTROL CHART METHOD

The following procedure is recommended for measuring the reliability, precision, and accuracy of chemical tests and analyses and for controlling the accuracy and precision of these tests during production.

Collect Data. Plan the check sample test procedure, designed to reveal all the variations to which production samples are subjected. Include all analysts and equipment in the test. Study all varying conditions, such as time, lighting, and temperatures, and submit samples as planned under as many conditions as possible. Record the results, time, analyst, equipment, and other identifying and pertinent data. When 50 to 100 check results have been obtained, analyze the data as shown below. In many cases it will be desirable to analyze the data after 20 values have been obtained, depending upon the rate of analyzing the check samples and the necessity for rapid installation of a control system. If only three or four results are obtained per day, the control chart may be started at the end of a week; but it should be revised after about 100 values are obtained. If the data are obtained much more rapidly, as is often the case in production laboratories, 100 values are obtained in a short time.

Group the Data. The first step in determining the state of control of the data is to group the data into related sections. In most cases this grouping is most useful when made on a chronological basis—that is, the data are divided into groups in the order in which the samples were submitted for analyses. The size of each group is usually varied between two and ten values per group, although larger groups may be used for special purposes.

The exact size of the group will be varied according to production conditions and statistical considerations. If it is desired to check the precision and accuracy each day and only two values are obtained each day, a group size of two will be useful.

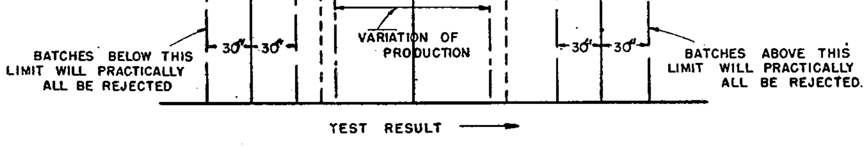


Figure 3. Comparison of Test Precision with Specifications and Production Variation

If the test is in continual use and a check sample is tested once an hour, groups of four or eight will allow a check twice or once each shift. In some cases it is desired to group the data according to analyst or equipment—for example, if there are ten testing stations in the plant and three check results are run at each station per day, groups of three per station would be a logical system of grouping. In general, the smaller the size of the group the more sensitive the chart becomes to individual variations. The larger the size of the group the more sensitive the test becomes on slight changes of the average.

Calculate Limits for Groups. Calculate the averages of all groups, $\bar{X}$'s, and the total average, $\bar{\bar{X}}$. Calculate the standard deviations of all groups, σ's, and the average standard deviation, $\bar{\sigma}$. In many cases the range is a good substitute for the standard deviation and involves less mathematics. However, when the groups are larger than four or five and the greatest efficiency is desired from a small amount of data, the standard deviation should be used.

Calculate the limits for the averages of the subgroups using the formula

$$\text{Limits for } \bar{X} = \bar{\bar{X}} \pm A_1\,\bar{\sigma} \qquad (12)$$

If the range is used in place of the standard deviation, use the formula

$$\text{Limits of } \bar{X} = \bar{\bar{X}} \pm A_2\,\bar{R} \qquad (13)$$

Calculate limits of standard deviation from the formula

$$\text{Limits for } \sigma = \left| \begin{matrix} B_3\,\bar{\sigma} \\ B_4\,\bar{\sigma} \end{matrix} \right. \qquad (14)$$

If the range is used, calculate limits for the formula

$$\text{Limits for } R = \left| \begin{matrix} D_3\,\bar{R} \\ D_4\,\bar{R} \end{matrix} \right. \qquad (15)$$

Test for State of Control. Compare all averages and standard deviations or ranges with the control limits. This is most easily done in the form of a control chart in which all group averages and standard deviations are plotted and the limits are shown by dotted lines. If any points are out of limits, this should be regarded as a sign of lack of control and the data in points out of control should be investigated, often an error or abnormal condition will be found. If causes for the points out of control are found, attempts should be made to prevent their affecting the test method in future. If this can be done, these out of control points may be eliminated from the data and the study continued.

Any points out of control limits must be regarded as a sign of lack of control and the method must be regarded as unreliable until causes of this abnormal variation are found.

If all points are within control limits, there is no evidence of lack of control. If 25 or more groups are all within control, we have reason to believe that the method is reliable.

Estimate the Precision of the Method. If the method is within control, we may proceed to estimate the precision of the method in terms of the universe standard deviation. This is done by means of formula:

$$\sigma' = \frac{\bar{\sigma}}{c_2} \qquad (2)$$

or

$$\sigma' = \frac{\bar{R}}{d_2} \qquad (16)$$

The limits of variation are then easily estimated from Formula 4. This may be expressed in relative terms by Formula 6.

Estimate the Accuracy of the Method. If the method has been found within control and the true value of the check sample is known, the accuracy of the method may be estimated in the following manner.

X, the known value, should be compared with the estimated true average of the test, $\bar{\bar{X}}$. We do not known the true average of the test, X', but we can determine within certain limits its probable value from the known average $\bar{\bar{X}}$ by Formula 9. Formula 9 should not be used if the data show lack of control.

If ***X*** is within the limits of uncertainty of X', the method should be regarded as accurate as far as the present data can determine. If ***X*** is outside these limits, it is highly probable that there is a constant error in the method and this constant error may be estimated by Formula 10.

Compare Accuracy and Precision of Test with Requirements of Process. The factors which determine the requirements of a routine test in chemical manufacture are:

1. The allowable variation in property being tested
2. The variation normally encountered in the property
3. The cost of a given magnitude of error in determining this property
4. Cost of more precise test methods
5. Availability of more precise methods

If the property being tested is a raw material, process control, or final product, a given amount of variation is allowed before action is taken. This band of allowed variation is usually called the specification limits or operating limits. The normal variation of the property being determined and the variation of the test are related to this limit width in the following way. If all the batches produced are normally made within specifications, the variation of the test should not be so great that some of these batches are reported out of limits.

The average of the characteristic of production lots $\pm 3\sqrt{(\sigma'\text{characteristic})^2 \pm (\sigma'\text{ test})^2}$ must fall within the limits if we are rarely to reject a normal (and within specification) datum.

We must also consider the possibility of abnormal variation in the property being tested. (In this case the property being tested has gone out of control and a control chart will soon catch this condition.) When this occurs we may make two possible errors—reject a good lot or accept a bad one. With a controlled analysis we know that the magnitude of these errors will practically never exceed $\pm 3\ \sigma'$ test. That means that with abnormal variation in the property being tested we shall sometimes accept a lot as far out of limits as $\pm 3\ \sigma'$ test and sometimes reject a lot as far as $\pm 3\ \sigma'$ test within the limits. The cost of making such errors as often as may be estimated from the frequency distribution must be considered (Figure 3).

When favorable indications are obtained from the above considerations, the method may be considered applicable to the requirements of the process. When costly errors are indicated, the cost of changing to more precise methods must be compared. In some cases more precise methods may not be known and the cost of making a test to fit the requirements is considered. When a better test cannot be found, we are faced with the possibility of (*a*) redesigning process—i.e., changing specifications, limits, methods of operation, material, etc.—(*b*) increasing number of tests, and (*c*) controlling property by other correlating factors.

In any case a comparison of this type will indicate the ability of the test to perform its function in the chemical process.

Table II. Viscosity of Cellulose Acetate Check Batch

Day	Viscosities, Seconds		$\bar{X}$	R	Day	Viscosities, Seconds		$\bar{X}$	R
1	71.0	71.0	71.0	0	26	77.0	74.5	75.75	2.5
2	74.0	74.0	74.0	0	27	72.0	71.0	71.5	2
3	75.5	76.5	76.0	1	28	73.0	73.0	73.0	0
4	75.0	74.0	74.5	1	29	77.0	74.0	75.5	3
5	70.0	68.5	69.0	1.5	30	77.0	72.0	74.5	5
6	72.5	67.0	69.25	4.5	31	75.5	73.5	74.5	2
7	77.0	77.0	77.0	0	32	77.0	77.5	77.25	0.5
8	71.5	69.0	70.25	2.5	33	78.0	78.0	78.0	0
9	74.0	72.0	73.0	2	34	76.0	73.5	74.75	2.5
10	72.5	73.5	73.0	1	35	76.0	76.0	76.0	0
11	77.5	75.0	76.25	2.5	36	77.0	72.5	74.75	4.5
12	74.5	72.0	73.25	2.5	37	75.5	73.9	74.25	2.5
13	74.5	76.5	75.5	2.0	38	75.5	73.5	74.5	2.0
14	73.5	75.0	74.25	1.5	39	74.0	76.0	75.0	2
15	75.0	77.0	76.0	2	40	74.5	75.0	74.75	0.5
16	75.0	73.5	74.25	1.5	41	79.5	76.5	78.0	3.0
17	75.5	74.0	74.75	1.5	42	76.0	75.0	75.5	1
18	75.0	75.0	75.0	0	43	75.0	78.0	76.5	3
19	77.5	74.0	75.75	3.5	44	73.0	73.0	73.0	0
20	74.0	76.5	75.25	2.5	45	75.0	74.0	74.5	1
21	70.0	69.0	69.5	1	46	75.0	71.0	73.0	4
22	74.0	75.0	74.5	1	47	76.5	75.0	75.75	1.5
23	72.0	74.0	73.0	2	48	75.0	75.0	75.0	0
24	75.0	74.5	74.75	0.5	49	75.5	76.0	75.75	0.5
25	75.0	75.0	75.0	0		Av.		74.45	1.6

$\bar{\bar{X}} = 74.45 \quad \bar{R} = 1.6 \quad n = 2$

$$\text{Limits of } \bar{X} = \bar{\bar{X}} \pm A_2\bar{R} = 74.45 \pm 1.88\,(1.6) = \left|\begin{matrix}77.5\\71.4\end{matrix}\right.$$

$$\text{Limits of } R = \left|\begin{matrix}D_4\bar{R}\\D_3\bar{R}\end{matrix}\right. = \left|\begin{matrix}3.27\ (1.6)\\0\ (1.6)\end{matrix}\right. = \left|\begin{matrix}5.5\\0\end{matrix}\right.$$

$$\text{Universe standard deviation } \sigma' = \frac{\bar{R}}{d_2} = \frac{1.6}{1.128} = 1.42$$

Continue to Control Accuracy and Precision of Test. The standard samples should be submitted to the test at intervals. It is usually desirable to submit them so that they cannot be distinguished from production samples because of the psychological bias which becomes established on known check samples This is especially important on tests demanding judgment or estimated readings, but less important on machine-made tests and tests in which the knowledge of the check sample cannot influence the results. The results should be plotted on a control chart as soon as they have been obtained. This can be done by the head analyst of each laboratory section, or by the analyst himself after the check sample has been identified by the head analyst. Results can be plotted as single determinations using control limits of $\pm 3\ \sigma'$, or if the results are obtained in groups of two or three, the group averages and ranges may be plotted. In any case, action should be taken any time a point is found to be outside of limits. The analyst and head analyst should seek to find the cause for lack of control. It is not sufficient to make a rerun within control; in fact, this will often occur even if the cause of lack of control is still present. Sometimes this presents a problem and it is up to the analyst to find the cause of the trouble, so that it can be eliminated as a cause of error in the production analyses. The control chart will not show the cause of the error, it can and does indicate as a practical certainty that some factor not in previous analyses has been introduced.

All results should be treated with suspicion when the control chart of any analysis shows lack of control until the cause is found and eliminated. Even then a period of probation in which the number and frequency of standard samples are increased is a wise precaution.

It is also helpful to run special check samples whenever standard solutions or equipment is changed, or when test equipment is started up after a period of shutdown.

The data of the control chart should be closely re-examined once a week or once a month, especially when the chart is set up on single values or groups of small size. The data may be regrouped in weekly or monthly groups and limits for these groups determined. This will detect small deviations from the average which may not be apparent on the original chart.

EXAMPLE. A viscosity test is used in the manufacture of cellulose esters. A large number of tests are run each day and for purposes of control it has been customary to run two tests per day on a known check batch. It is desired to study this test and to safeguard quality by controlling the accuracy and precision of this test.

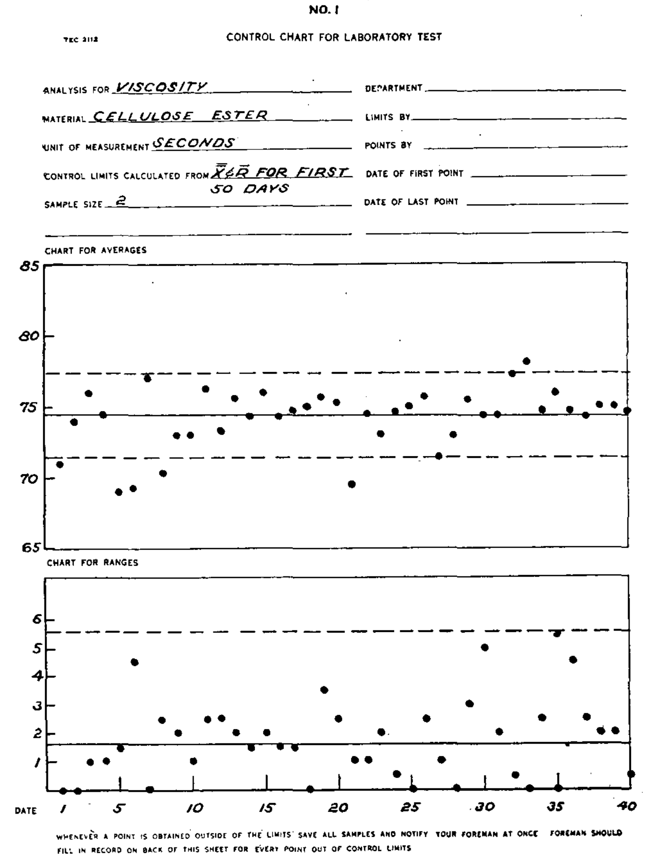
I. It is a simple matter to obtain data for the past 49 days on the check batch results and to prepare a control chart on this date (Table II).

II. The data may be logically grouped into groups of two, since two results were obtained on each day. It would seem a reasonable goal to obtain no more variation from day to day than was obtained in any one day.

III. The range may be used as the measure of precision and limits calculated for $\bar{X}$ and R, as in Table II.

Table III. Application of Control Chart Method to Industrial Tests and Analyses

Test Method or Analysis	Material Tested	State of Control When First Charted	After Use of Control Chart: Reliability	After Use of Control Chart: Accuracy (relative constant error), %	After Use of Control Chart: Precision (relative limits of variation), %	Comments
Viscosity	Cellulose acetate	Lack of control	In control	...	±4.6	Satisfactory for purpose
Acetic acid	Acetic acid	Lack of control on some laboratories	In control	0 within known limits	±0.25	Satisfactory for purpose
Butyryl content	Cellulose acetate butyrate	In control	In control	0 within known limits	±4	Limits of variation too wide for specification. Must be controlled by other method
Butyric anhydride	Butyric anhydride	In control	In control	0 within known limits	±2	Satisfactory for purpose
Sulfuric acid	Mixed acid solution	Lack of control	In control	+4	±8	Accuracy and precision unsatisfactory for purpose. New type of test required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TEC 2112 CONTROL CHART FOR LABORATORY TEST

ANALYSIS FOR VISCOSITY

DEPARTMENT

MATERIAL CELLULOSE ESTER

LIMITS BY

UNIT OF MEASUREMENT SECONDS

POINTS BY

CONTROL LIMITS CALCULATED FROM $\bar{\bar{X}}$ & $\bar{R}$ FOR FIRST 50 DAYS

DATE OF FIRST POINT

SAMPLE SIZE 2

DATE OF LAST POINT

WHENEVER A POINT IS OBTAINED OUTSIDE OF THE LIMITS SAVE ALL SAMPLES AND NOTIFY YOUR FOREMAN AT ONCE FOREMAN SHOULD FILL IN RECORD ON BACK OF THIS SHEET FOR EVERY POINT OUT OF CONTROL LIMITS

Figure 4. Control Chart for Laboratory Test

IV. The control chart, Figure 4 shows decided lack of control. Some factors are causing considerably more variation from day to day than is present in any one day. Such causes can be removed or minimized by scientific investigation, and this must be done before the test can be considered reliable.

The test was investigated and all analysts were asked to check weighings more carefully and to maintain accurate adjustments of temperature. No specific cause of errors was found, but a number of weak details were revised in a better procedure.

Further data were obtained and it soon became evident that the average viscosity now obtained was 75.5 seconds and an average range for the groups of two was 1.3 seconds for about 50 points, all within control. A portion of these data is shown in Figure 5. These data now show control and may be considered reliable.

V. The precision of the test may be measured by the estimated standard deviation:

$$\sigma' = \frac{\bar{R}}{d_2} = \frac{1.3}{1.128} = 1.15$$

The limits of variation may be estimated by:

$$\bar{X} \pm 3\sigma' = 75.5 \pm 3(1.15) = \begin{vmatrix}79.0\\72.0\end{vmatrix}$$

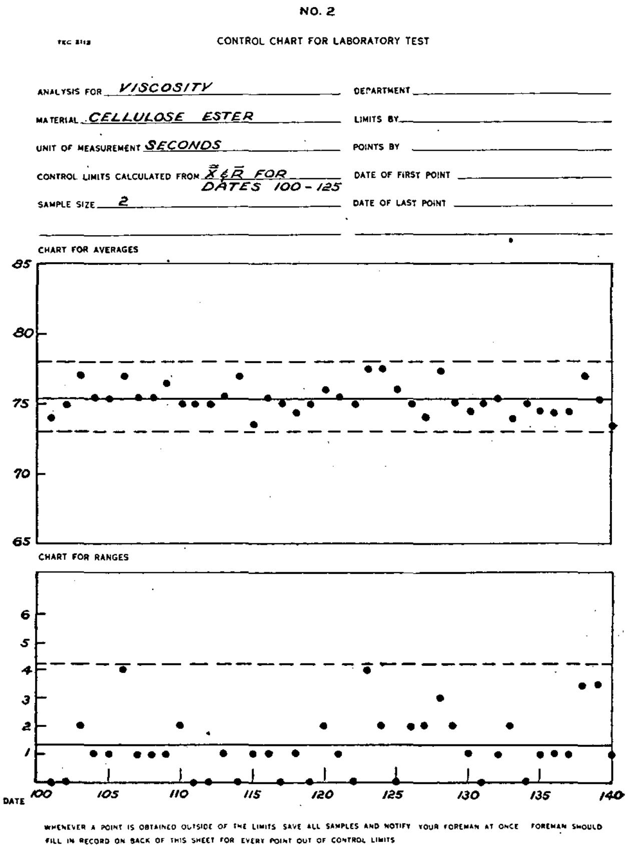
VI. No concept of absolute accuracy is applicable to this test, since the test is a relative measure of viscosity and the check sample has not been assigned a standard value. The viscosity of the check batch as determined by this method is now known within relatively close limits. These limits of error may be estimated by:

$$\text{Limits of } X' = \bar{\bar{X}} \pm 3\frac{\sigma'}{\sqrt{N-3}} =$$

$$75.5 \pm 3\frac{1.15}{\sqrt{100-3}} = \begin{vmatrix}75.8\\75.2\end{vmatrix}$$

If a standard value for this test sample were known it could be compared with this range, and if included, the method should be considered accurate within the limits. If not included, a constant error is indicated. This range of viscosity may not be used to define the viscosity value of the check sample for standardization.

VII. In order to compare the accuracy and precision of this test with the requirements of the process, we must compare these


NO. 2

TEC 2112 CONTROL CHART FOR LABORATORY TEST

ANALYSIS FOR VISCOSITY

DEPARTMENT

MATERIAL CELLULOSE ESTER

LIMITS BY

UNIT OF MEASUREMENT SECONDS

POINTS BY

CONTROL LIMITS CALCULATED FROM $\bar{\bar{X}}$ & $\bar{R}$ FOR DATES 100 - 125

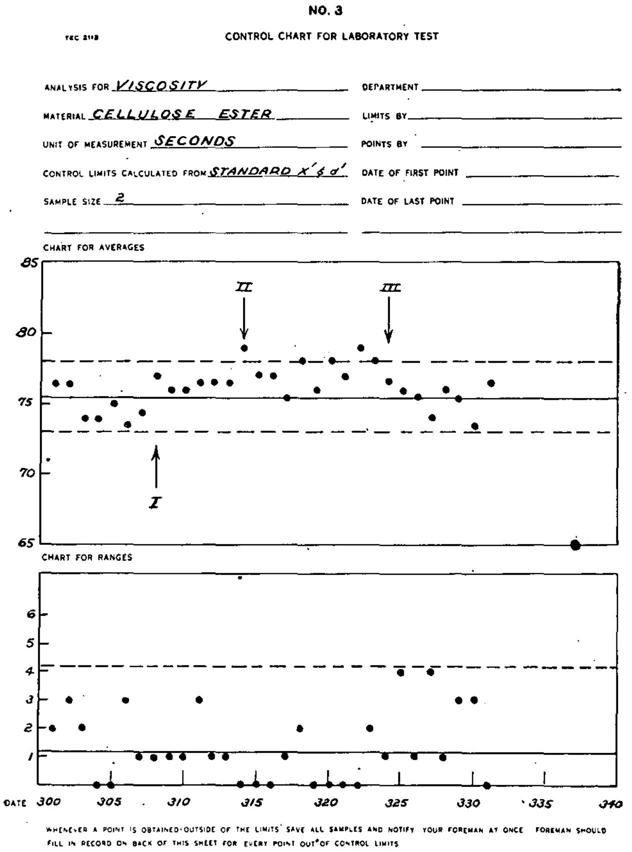
DATE OF FIRST POINT

SAMPLE SIZE 2

DATE OF LAST POINT

WHENEVER A POINT IS OBTAINED OUTSIDE OF THE LIMITS SAVE ALL SAMPLES AND NOTIFY YOUR FOREMAN AT ONCE FOREMAN SHOULD FILL IN RECORD ON BACK OF THIS SHEET FOR EVERY POINT OUT OF CONTROL LIMITS

Figure 5. Control Chart for Laboratory Test



NO. 3

TEC 2118

CONTROL CHART FOR LABORATORY TEST

ANALYSIS FOR VISCOSITY	DEPARTMENT
MATERIAL CELLULOSE ESTER	LIMITS BY
UNIT OF MEASUREMENT SECONDS	POINTS BY
CONTROL LIMITS CALCULATED FROM STANDARD X′ & σ′	DATE OF FIRST POINT
SAMPLE SIZE 2	DATE OF LAST POINT

WHENEVER A POINT IS OBTAINED OUTSIDE OF THE LIMITS SAVE ALL SAMPLES AND NOTIFY YOUR FOREMAN AT ONCE FOREMAN SHOULD FILL IN RECORD ON BACK OF THIS SHEET FOR EVERY POINT OUT OF CONTROL LIMITS

Figure 6. Control Chart for Laboratory Test

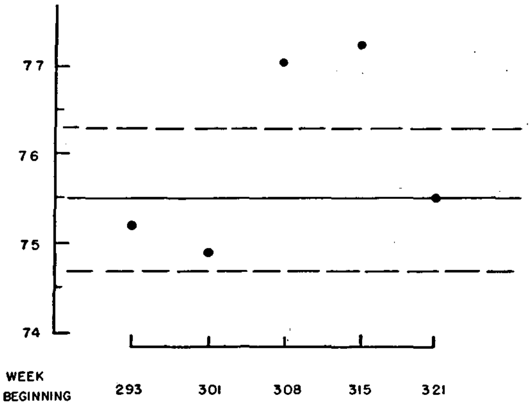


Figure 7. Weekly Average Viscosity of Check Samples

values with the variation of the product normally encountered and the specification limits. In this case the specifications required the batches to be within a range of 60 to 90 seconds. The variation of the production had been determined from a previous study and is expressed as:

$$\bar{\bar{X}} = 76$$

$$\sigma' = 3.0$$

(These figures express the actual variation of production and do not include variation from test.)

The total expected variation of the test results of production is therefore:

$$76 \pm 3\sqrt{(1.15)^2 \pm (3.0)^2} = 76 \pm 3\sqrt{10} = 76 \pm 9.5 = \left|\begin{matrix}85.5\\66.5\end{matrix}\right.$$

A normal batch will, therefore, not be rejected as a result of variation in this test. There is always the possibility that the production process will go out of control or that an abnormal batch will appear. Since this may produce a batch at any value, we may expect the test to make an incorrect classification of a batch in borderline cases. With the accuracy of this test, we can sometimes expect to pass a batch outside of specifications as far as 60 − 3 (1.15) and 90 + 3 (1.15) or to reject a batch which is actually inside the specifications as far as 60 + 3 (1.15) and 90 − 3 (1.15). If this is a serious error, the test should be judged inadequate. In this case it is not a serious error and the test may be judged satisfactory. This situation is illustrated in Figure 3.

VIII. The check sample continued to be submitted to the test and a number of times later showed lack of control. These cases enabled the analysts to locate and eliminate a number of sources of error.

One of these cases is shown in Figure 6. A point out of control was first noticed on day 314, but no cause was found. Again on day 322, a second point out of control was revealed. The general high trend appeared significant and this was confirmed when the averages for the week were plotted on a weekly control chart (Figure 7). Persevering investigation revealed the fact that a change in the source of the solvent used in the test had occurred on day 308. This brought about a return to the original source material on day 324. Notice the returned state of control. This evidence revealed a cause of variation the analysts were able to investigate further and eliminate as a cause of variation.

This example illustrates the use of the control chart method in considerable detail. The method is applicable to other types of tests and production conditions. The exact details can and should be varied to meet specific requirements.

Table III shows a summary of several analytical procedures which have been subjected to this type of statistical investigation and control and may serve as a guide in other problems. The first test listed is the one given in the detailed example.

CONCLUSION

The use of statistical methods in the study of production control tests and analyses is an important aid in assuring the reliability of the results obtained and therefore in the maintenance and improvement of the quality and efficiency of the production process. It is a fundamental step in any quality control program. The proper selection and use of test methods are as important in the design of the production process as any other critical step in the procedures. It is hoped that this description of one application of this method will aid the chemist, analyst, chemical engineer, and production supervisor to measure and control the reliability, accuracy, and precision of control tests. The details presented in this paper should be utilized as a guide and not necessarily followed exactly. Experience and ingenuity will soon reveal methods of application of greatest value in any particular field.

ACKNOWLEDGMENT

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Trends in Quantitative Analysis

A Survey of Papers for the Year 1946

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In order to help decide what methods of quantitative analysis will be important in the future and to compare future use of classical and newer instrumental methods, all research papers published in 1946 and covered in *Chemical Abstracts* prior to September 1947 were studied. Though the largest number of papers is on titrimetry (volumetric analysis), the number on colorimetry is almost as great; 56% of all papers are on instrumental methods of analysis, principally colorimetry, spectrophotometry, emission spectrography, instrumental titrimetry, and polarography; among preliminary steps described by research papers, chromatography is numerically outstanding; next to English, more 1946 papers are written in Russian than in any other language; 58% of the papers devoted to quantitative analysis during 1946 are concerned with the determination of organic compounds.

COLUMNS and editorials in ANALYTICAL CHEMISTRY and the correspondence they quote show that many chemists are asking, "Where is analytical chemistry heading, technically and professionally?" This paper is concerned with the technical side of the question applied to quantitative analysis.

Though many teachers of quantitative analysis are adding as much material on the newer instrumental methods of analysis as time and equipment permit (*1*, *4*, *6*, *9*), there are many shades of opinion on what is significant enough to include and whether the new methods are important enough to be given at the expense of material on the classical methods. Some teachers of analysis, either willingly or unwillingly, leave instruction in physicochemical methods of analysis to courses in physical chemistry. The uncertainty about what to teach is reflected in the number of queries addressed to Müller's column on "Instrumentation" in ANALYTICAL CHEMISTRY (*11*).

Because facts are of greater value than opinions, a convenient and objective indication of the future practical importance of the various analytical methods can be obtained by a statistical study of the research papers now appearing in the journals. To some extent, the present importance of a method can also be measured, since many papers describe improvements of procedures now in wide use. Of course, conclusions must be drawn with care; not all discoveries and improvements will be adopted, and those that are adopted will not be equally valuable. Keeping these limitations in mind, partial answers to the above questions can be obtained. Better answers could be given if similar studies could be made periodically and then correlated with one another and with industrial practice. However, no recent paper of this sort that would permit correlation could be found.

With very little additional labor, other useful or at least interesting information is obtainable from a literature survey, and is presented in this paper.

Consider first the languages in which the papers are written. There is much discussion in educational circles today of the relative importance to scientists of the various languages, especially Russian (*2*, *7*). Though this study is limited to only very recent publications in the field of quantitative analysis, it can yield data of value in discussing this question. Also of interest but strongly affected by the war is a list of countries in which the research was done, with a total of papers from each. Furthermore, a rough estimation of the proportion of 1946 papers which are on quantitative analysis can be made by combining the data of this survey with those of Crane (*3*) on the number of abstracts that have appeared each year in *Chemical Abstracts*. Lastly, in order to see whether modern quantitative analysis is more concerned with determining organic or inorganic substances, a count can be kept of this aspect. The present trend is toward making organic analysis part of analytical chemistry rather than organic chemistry (*10*).

PROCEDURE

General. The most convenient period for a survey of papers is a complete year, and in order to cover as recent a period as possible, 1946 was chosen. The main source of material was, naturally, *Chemical Abstracts*. Since its index is not designed for such a search, it was necessary to skim briefly through each page, omitting a few sections very unlikely to contain analytical papers. It is possible that a few were missed. At times more were found outside Section 7 than in it. Summer issues of *Chemical Abstracts* for 1947 show a decrease to a small fairly constant number of 1946 papers. An arbitrary stop was made with No. 16, 1947, because it was felt that it would be some time before 1946 papers ceased appearing entirely and the relative results would probably be unaffected by a delay in the summation of results. When the abstract of a paper did not give sufficient information to classify it, the paper itself was consulted if available.

To be included in the study, a paper had to be concerned, in whole or in part, with quantitative analysis. It could be a complete determination or a step such as sampling, filtration, or distillation, provided that it was specifically applied to analysis. Also included were patents on analytical apparatus and reviews of methods. Reports of analyses by known methods were not included if they did not contain significant research on the methods used.

As for the nomenclature used in the tables, the author feels that a paper of this sort is not the place to standardize terminology. Rather, all terms found to be in general use in the papers surveyed should be given. In no case did the number of interchangeable terms exceed two. Equivalent terms are given in parentheses in the tables and throughout the discussions. When a group name was desired and could not be found in the papers, the terminology of *Chemical Abstracts* was followed. Some method names—e.g., chronometric, microscopical—were taken from Kolthoff and Sandell (*8*).

Classification of Papers According to Method Used. Some papers contained research on more than one method, usually a comparison. If the methods were in different classifications—e.g., colorimetry and gravimetric analysis—the paper was counted in both classifications. Classifications given at the bottom of Table I were not included in the calculations. Therefore the total of figures in column 2 is not the same as the total number of papers covered by the survey. The percentage of papers in each classification (column 3) was calculated from the column 2 total. When large numbers of methods of different types were covered in one paper (extensive reviews, collected official methods, etc.), the paper was called "many methods" and no addition was made to the figures for those methods; it was felt that they did not deserve the weight of papers entirely on one or two methods. A classification of "preliminary steps and methods of sepa-

Table I. Classification of Analytical Papers According to Method

Methods	No. of Papers	% of Total
Titrimetry (volumetric analysis)	323	25.6
Colorimetry	291	23.0
Gravimetic analysis	108	8.5
Spectrophotometry	72	5.7
Emission spectrography and automatic spectrometry (the latter a new method)	67	5.3
Polarography	51	4.0
Biological assay	46	3.6
Miscellaneous methods	32	2.5
General quantitative analysis	29	2.3
Manometric methods	22	1.7
Combustion analysis	21	1.7
Mass spectrometry and spectrography	21	1.7
Fluorometry	20	1.6
Gas analysis	18	1.4
Absorption spectrometry and spectrography	17	1.3
Turbidimetry	14	1.1
Tracer analysis (radioactive and nonradioactive isotopes)	14	1.1
Densitometry	11	0.9
Emission flame photometry, spectrophotometry, and spectrography	7	0.6
X-ray diffraction spectrography	7	0.6
Thermal conductivity	6	0.5
Refractometry	6	0.5
Electroanalysis	6	0.5
Microscopical analysis	6	0.5
Chronometric methods	5	0.4
Electrical conductivity	5	0.4
Volume of liquid distilled (including entrainment methods)	5	0.4
Critical solution temperature (cloud point)	4	0.3
Nephelometry	4	0.3
Raman spectrography	4	0.3
Viscometry (viscosimetry)	3	0.2
Melting point and freezing point	3	0.2
Thermometric analysis	3	0.2
Volume of precipitate	2	0.2
Dispersion	2	0.2
Magnetic susceptibility	2	0.2
Optico-acoustical analysis	2	0.2
Polarimetry	2	0.2
Capillary analysis	2	0.2
Electrographic analysis (new method)	1	0.1
Neutron capture (new method)	1	0.1
Evolution	1	0.1
Total	1266	100.4

Not included: papers on preliminary steps and separation methods (107), many methods (43), unclassified (36).

Table II. Instrumental *vs.* Noninstrumental Methods

Noninstrumental Methods		No. of Papers
Titrimetry (volumetric analysis), visual		251
Gravimetric analysis		108
Biological assay		46
Colorimetry, matching		34
	Total	439
Instrumental Methods		
Colorimetry[a]		
Photoelectric	133	202
Visual, instrumental	69	
Spectrophotometry		72
Emission spectrography		67
Titrimetry (volumetric analysis)		
Potentiometric	41	60
Amperometric	11	
Conductometric	6	
Thermometric	2	
Polarography		51
Combustion		21
Mass spectrometry and spectrography		21
Fluorometry		20
Gas analysis		18
Absorption spectrometry and spectrography		17
Turbidimetry		14
	Total	563
Summary		
Noninstrumental		439
Instrumental		563
	Total number of papers	1002

[a] 48 papers on colorimetry were not classified as either instrumental or noninstrumental. Probably they would almost all be found instrumental.

ration" was created to contain papers on such subjects as sampling, filtration, extraction, etc.

Papers classified as miscellaneous were principally on complex methods for which no name has been proposed and which could not be described by a short phrase. Papers announcing new methods of analysis were so designated in Table I.

Papers on the Dumas determination of nitrogen were classified as "combustion" papers rather than "manometric (gasometric)" as is sometimes done. Since carbon-hydrogen combustion determinations may be concluded by either weighing or titration, but are not classified as "gravimetric" or "titrimetric," this seemed to be more logical. Papers on the determination of carbon in steel by combustion were counted under combustion.

Kjeldahl determination papers were counted under both "titrimetric-visual" and "separation methods–distillation."

The titrimetric method of Jensen and Parrock has been given no specific name and hence was counted as conductometric. It is a new method.

Instrumental *vs.* Noninstrumental Methods. As pointed out by Müller (*12*), a truly instrumental method is entirely automatic, from putting in the sample to getting the result "printed on a ticket." However, though colorimeters are seldom made direct-reading, we think of a determination with a colorimeter as intrinsically instrumental. Hence, for want of a better term, "instrumental" was taken to refer to such methods as spectrophotometry, colorimetry, and polarography. Table II was compiled to compare the number of papers on classical noninstrumental methods with those on the newer instrumental methods. Because of difficulty in classifying some of the less numerous methods, they were omitted; their number is so small that their effect on the result would be negligible.

Subdivisions of papers on preliminary steps were made in Table III. To be consistent with the practice of counting a paper on two methods under both methods, it seemed necessary to take note of papers describing research on a determination where the novel feature lay in a preliminary step. Such papers were counted under both the specific preliminary step and the final analytical method used. This accounts for the large number of papers covered in Table III, while the number listed at the bottom of Table I under "preliminary steps and separation methods" is small, since those included there were general in nature and applied to no specific method of determination.

Compilation of Tables IV, V, and VI was simple and straightforward. Some papers had to be classified in both groups in Table VI.

Table III. Classification of Papers on Preliminary Steps and Separation Methods

Preliminary Step or Separation Method		No. of Papers	% of Total
Adsorption			
Chromatography	45	62	28.6
Ion exchange	9		
Other	8		
Extraction		40	18.4
Precipitation		39	18.0
Distillation		22	10.3
Miscellaneous		15	6.9
Sampling		10	4.6
Filtration		7	3.2
Digestion (wet oxidation)		6	2.8
Complex ion formation		4	1.8
Reduction		4	1.8
Centrifuging		3	1.4
Dissolving		3	1.4
Dialysis		2	0.9
Total		217	100.1

Table IV. Languages of Analytical Papers

Language	No. of Papers	% of Papers
English	870	66.2
Russian	153	11.6
French	137	10.4
Spanish	57	4.3
Italian	31	2.4
German	23	1.7
Swedish	19	1.4
Dutch (Flemish)	16	1.2
Danish	3	0.2
Japanese	2	0.2
Norwegian	1	0.1
Czech	1	0.1
Jugoslavian	1	0.1
Total	1314	99.9
Unclassified	22	

CALCULATION AND DISCUSSION OF RESULTS

The total number of quantitative analysis research papers found to be published in the year 1946 was 1336. Of these, 34 are patents. A small number of 1946 papers are bound to appear in coming issues of *Chemical Abstracts*, but in order to apply the results to the future, it is necessary that 1946 be not too far in the past. The relative results should not be affected by this omission, except to increase slightly the percentage of foreign articles.

Turning first to Crane's (*3*) graph of papers abstracted each year in *Chemical Abstracts*, if we reduce the figure for papers abstracted last year to allow for the acquisition of back number journals unobtainable during the war, we arrive at the approximate figure of 35,000 papers deemed suitable for inclusion in *Chemical Abstracts*. Making the assumption that this number is roughly the same as the number published in 1946, we can compare this with the 1336 analytical papers found by this survey and conclude that 1 paper in 26 is on quantitative analysis research. This is rather interesting, though not of great significance.

Methods of Quantitative Analysis. The most striking part of Table I is the high standing of colorimetry, a close second to titrimetry (volumetric analysis). Combining it with its close relative, spectrophotometry, puts the combination in first place. It is raised still more if the closely related classification of absorption spectrometry and absorption spectrography is included. The high standings of emission spectrography, polarography, and biological assay are worthy of note. This table should prove useful in revamping the content of advanced courses in quantitative analysis.

Instrumental *vs.* Noninstrumental Methods (Table II). The fact that 56% of 1946 analytical papers are on instrumental methods of analysis indicates their future practical importance. Colorimetry, spectrophotometry, emission spectrography, instrumental titrimetry (volumetric methods), and polarography show up as the "big five." On the other hand, it must be admitted that noninstrumental methods will probably be widely used for some time to come.

Preliminary Steps and Separation Methods (Table III). The usual separation methods (extraction, precipitation, distillation, and filtration—in order of frequency) are topped by adsorption, with chromatography the principal subdivision. So many 1946 papers are on chromatography that it is reasonable to recommend that advanced analytical courses contain class and laboratory instruction in this important method of separation. The preliminary step receiving the greatest attention is sampling.

Languages in Which Analytical Papers Are Written. The contention that knowledge of the Russian language is and will be important to analytical chemists is borne out by Table IV; Russian papers are next to English in frequency, though one sixth of their number. French is a close third. The theory that because of Russia's economic problems, its research would be thoroughly practical in nature, was found untrue in analytical chemistry, numerous theoretical papers of high caliber being noted. Of course, in evaluating the importance of a language to chemists, the extent of past literature as well as of the present and future must be considered. This consideration applies especially to Russian and German. The huge quantity of captured German research reports together with previously available German literature will serve to maintain for some time its position as the foreign language of greatest use to English-speaking chemists (*5*).

Table V. Countries in Which Research for Papers Was Done

Country	No. of Papers	% of Papers
United States	549	41.6
Great Britain	192	14.6
Union of Soviet Socialist Republics	162	12.3
France	105	8.0
Sweden	43	3.3
Italy	33	2.5
Switzerland	31	2.4
Spain	29	2.2
Netherlands	24	1.8
India	23	1.7
Australia	19	1.4
Canada	14	1.1
Belgium	13	1.0
Argentina	12	0.9
Brazil	12	0.9
Denmark	10	0.8
Northern Rhodesia	7	0.5
New Zealand	4	0.3
Finland	4	0.3
Union of South Africa	3	0.2
Germany	3	0.2
Norway	3	0.2
Greece	2	0.2
Hawaii	2	0.2
Chile	2	0.2
Romania	2	0.2
Japan	2	0.2
Jugoslavia	2	0.2
Czechoslovakia	2	0.2
Mexico	1	0.1
China	1	0.1
Palestine	1	0.1
Peru	1	0.1
Puerto Rico	1	0.1
Egypt	1	0.1
Hungary	1	0.1
British West Indies	1	0.1
Irish Free State	1	0.1
Total	1318	100.5
Unclassified	18	

Table VI. Division of Papers According to Nature of Substance to Be Determined

Nature of Substance	No. of Papers	% of Papers
Organic	654	58
Inorganic	473	42
Total	1127	100

Metal organic (8), general (168), unclassified (16).

Countries in Which Research for Papers Was Done. Table V requires little comment. Present dominance of the United States is evident. Following Great Britain but well ahead of France is the Soviet Union. Sweden is in fifth place.

Organic *vs.* Inorganic Substances. The previous conviction of this author concerning the importance of the quantitative determination of organic compounds is verified by Table VI, which shows that the majority of 1946 papers were on the determination of organic compounds. Though it is probably correct to attribute this partly to the existence of many satisfactory methods for the determination of inorganic substances, it seems justifiable to conclude that teachers of analytical chemistry should place more emphasis on quantitative organic analysis than at present and not leave instruction in this growing branch of analysis to the teacher of organic chemistry.

SUMMARY

A statistical survey of quantitative analysis research papers published in 1946 uncovered the following facts: Though the largest number of papers are in the classical field of volumetric analysis or titrimetry, colorimetry is a close second, and if combined with those on the very similar method of spectrophotometry, exceeds every other method. Instrumental methods of analysis comprise 56% of all papers, the first five being (in decreasing order) colorimetry, spectrophotometry, emission spectrography, instrumental titrimetry (volumetric analysis), and polarography. Statistically outstanding steps preliminary to the final determination are (in decreasing order) adsorption (especially chromatography), extraction, precipitation, distillation, sampling, and filtration. Next to English, the language in which most 1946 analytical papers are written is Russian; French, Spanish, and Italian follow in that order. Tabulation of the countries in which the research for papers was done gives, in decreasing order, United States, Great Britain, U.S.S.R., France, Sweden, etc. More than half of the papers (58%) are on the determination of organic compounds.

ACKNOWLEDGMENT

The author is indebted to Earl J. Serfass for his interest in the progress of this paper and for his helpful advice and criticism.

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RECEIVED October 6, 1947.

Determination of Olefinic Unsaturation

Cooperative Evaluation of Nitrogen Tetroxide Methods

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G. R. BOND, JR., *Houdry Process Corporation of Pennsylvania, Wilmington, Del.*, AND COOPERATORS[1]

Two standardized procedures for the determination of olefins by reaction with nitrogen tetroxide were cooperatively evaluated by an A.S.T.M. group. The results of this work indicate that the methods give a satisfactory value for total olefin content of hydrocarbon mixtures in the gasoline boiling range which contain other than highly branched olefins. Further work is planned on highly branched olefins of the di- and triisobutylene type. The need for estimating olefin molecular weights, required with bromine number methods, is eliminated. Method A provides an olefin-free portion of the test sample which is suitable for additional analysis for other hydrocarbon types. Future work will further improve the precision and accuracy of the methods and extend their applicability to highly branched olefins.

DURING the war, Subcommittee XXV was organized under Committee D-2 of the American Society for Testing Materials for the purpose of developing methods of analysis of petroleum products for hydrocarbon types. Of particular interest to this group was the reaction of nitrogen tetroxide with olefin hydrocarbons as a possible basis for a procedure for quantitative determination of the olefin content of hydrocarbon mixtures. Previous work by Bond (*3*) indicated that, under certain prescribed conditions, nitrogen tetroxide was void of the conflicting reactions associated with halogen titration procedures, and two general procedures utilizing nitrogen tetroxide were outlined which were proposed as possible replacements for, or supplements to, the commonly used bromine number methods for determination of olefins.

The evaluation and standardization of these procedures were placed under the jurisdiction of Section B of Subcommittee XXV. The work undertaken by this section involved (1) improvement of the design of apparatus and operating technique, and (2) cooperative evaluation of standardized procedures as test methods for determination of olefins. Nine laboratories cooperated in this phase of the work.

The present paper presents in some detail the present status of the development work, and the limitations and precisions of the methods as interpreted from the data and contributions of the cooperators.

OUTLINE OF METHODS

Method A. Steam-Distillation Procedure. Gaseous nitrogen tetroxide is passed into the chilled sample to react with the olefins. At the end of the reaction, an aqueous solution of urea is added to decompose the excess nitrogen tetroxide. The mixture is steam-distilled, the unreacted hydrocarbons being removed as the distillate. The content of total olefins is obtained from the difference in volume of the unreacted hydrocarbons and the volume of the original sample.

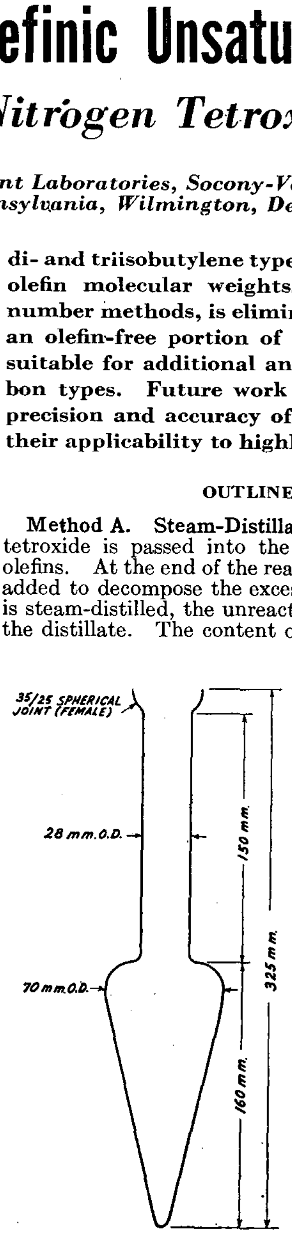

Figure 1. Treating-Distilling Flask

This procedure, in addition to determining the olefin content, produces an essentially olefin-free portion of the sample, which may be used for determination of other hydrocarbon types.

Method B. Direct Volumetric Procedure. Gaseous nitrogen tetroxide is passed into the chilled sample to react with the olefins. The nitrosates formed react with alcoholic potassium sulfide solution, permitting the measurement of the unreacted portion of the test sample. The content of total olefins is obtained from the difference in volume of the unreacted portion of the test sample and the original volume of test sample.

This method is applicable where only the total olefin content of the sample is required.

---

[1] E. L. Baldeschwieler, Standard Oil Development Co.
L. M. Henderson, Pure Oil Co.
S. S. Kurtz, Jr., Sun Oil Co.
H. Levin, The Texas Co.
C. E. Starr, Standard Oil Co. of New Jersey, Louisiana Division
E. B. Tucker, Standard Oil Co. of Indiana
F. D. Tuemmler, Shell Development Co.

Table I. Composition of Synthetic Blends of Olefins for Cooperative Testing in A.S.T.M. D-2 XXV-B

Components	B-5		B-6		B-7		B-8	
	Vol. %	Wt. %	Vol. %	Wt. %	Vol. %	Wt. %	Vol. %	Wt. %
Hexene-3	1.0	0.9	1.0	0.9	0.5	0.5	...	...
Octene-1	6.9	6.7	8.0	7.6	14.0	13.4	...	...
Decene-1	3.0	2.9	4.0	4.0	5.0	5.0	...	...
Diisobutylene	...	...	...	...	...	...	12.0	11.6
Nonenes (mixed)	...	...	...	...	...	...	6.0	6.0
Cyclohexene	...	...	2.0	2.2	6.5	7.0	...	...
2-Methylpentadiene	...	...	2.0	1.9	1.5	1.4	...	...
α-Methylstyrene	...	...	2.0	2.4	1.5	1.8	...	..
Oklahoma City naphtha, straight-run	89.1	89.5	81.0	81.0	71.0	70.9	82.0	82.4
Totals	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total olefins	10.9	10.5	19.0	19.0	29.0	29.1	18.0	17.6
Total olefins, av. mol. wt.	115		107		104		116	

Table II. Properties of Olefins Used in A.S.T.M. Cooperative Samples B-5 to B-8

Sample	Density, d²⁰	Refractive Index, n_D^{20}	Bromine No. by Method ES-45a	Specific Dispersion	Theoretical Bromine No.	Literature Values		
						Density d²⁰	Refractive index, n_D^{20}	Reference
Hexene-3	0.6890	1.3986	174	133.2	189.8	*cis*-0.6796	1.3934	(*1*)
						trans-0.6779	1.3938	(*1*)
2-Methylpentadiene	0.7183	1.4469	234	226.8	388.8	0.719	1.446	(*1*)
α-Methylstyrene	0.9092	1.5381	135	...	135.2	0.9106	1.5386	(*1*)
Diisobutylene	0.7177	1.4100	149	122.2	142.4	....	....	..
Decene-1	0.7413	1.4214	110	113.6	113.9	0.7396	1.4220	(*4*)
Octene-1	0.7158	1.4083	139	117.1	142.4	0.7160	1.4088	(*1*)
Cyclohexene	0.8106	1.4463	182	119.0	194.4	0.8108	1.4467	(*4*)
Mixed nonenes	0.7502	1.4251	123	116.5	126.5	....	....	..

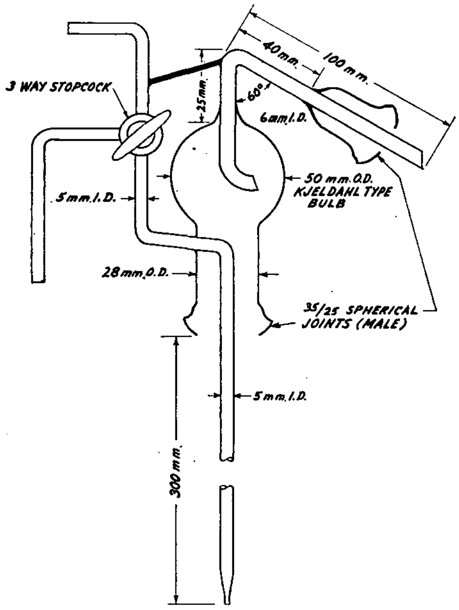

Figure 2. Adapter

METHODS USED IN COOPERATIVE WORK

The analytical procedures used in the cooperative work were essentially those described in a previous publication (*3*), with the following exceptions:

Method A. APPARATUS. The apparatus was designed to minimize handling and distillation losses, since Method A requires careful volume measurements to determine olefins by difference. This apparatus, constructed of glass, included a treating-distilling flask (Figure 1), an adapter for connecting the flask to the steam-distillation setup (Figure 2), an efficient condenser, and a product receiver assembly.

Two types of product receivers were tested cooperatively. Type 1 (Figure 3) consisted of a water trap for nitrosates, a separatory funnel for collecting the steam-distilled product, and a dry ice aftercondenser to minimize loss of product by vaporization. Type 2 receiver (Figure 4) was essentially the same design as that described in a previous publication (*3*).

REAGENTS. Urea or sulfamic acid solution was recommended for destroying the excess nitrogen tetroxide after treatment of the sample. Urea solution was used by most of the cooperators.

ALCOHOLIC SOLUTIONS OF REAGENTS. Most of the cooperative work was obtained with ethanol solutions of reagents, but more recent work has indicated that methanol is more suitable, since the ethanol solutions of sodium hydroxide or potassium hydroxide darken on standing.

PROCEDURE. With the use of Type 1 product receiver, the steam-distillation procedure was as follows:

The flask containing the treated sample was connected to the assembled condenser and product receiver Type 1 (Figure 3). The separatory funnel containing a few milliliters of water was surrounded with an ice water bath, the nitrosate trap filled with water, and the aftercondenser filled with dry ice. The steam-distillation was carried out by immersing the distilling-treating flask in boiling water and introducing steam through the three-way stopcock of the adapter (Figure 2), until the distillate became heavier than water and settled to the bottom of the nitrosate trap. The unreacted hydrocarbon, after the water had been drawn off, was shaken with 10 ml. of alcoholic sodium hydroxide solution. Water was then added, the mixture agitated and allowed to settle, and the aqueous layer drawn off. Measurement of the volume of the hydrocarbon layer was carried out as described (*3*).

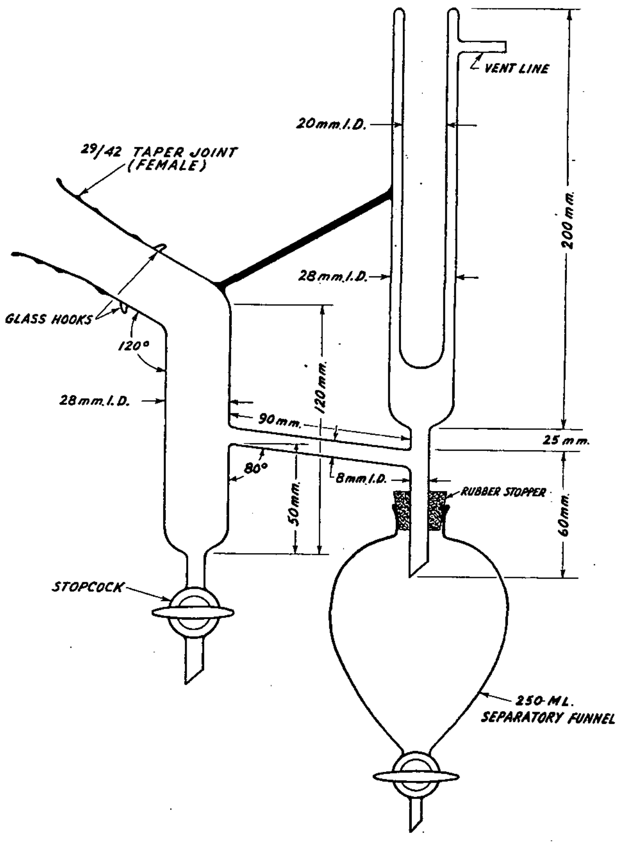

Figure 3. Product Receiver Assembly, Type 1

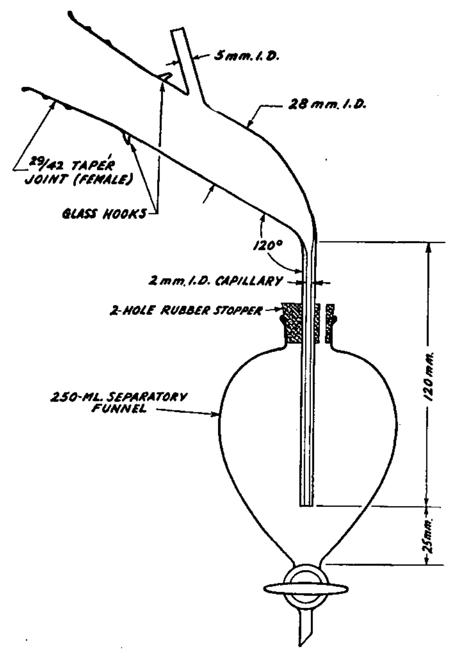

Figure 4. Product Receiver Assembly, Type 2

In the use of Type 2 product receiver, a slow stream of air was passed into the side tube of the adapter, just sufficient to overcome the hydrostatic pressure in the separatory funnel receiver. The procedure given in a previous publication (*3*) is considered equally satisfactory.

In the cooperative work only the alcoholic sodium hydroxide and water washes were applied to the hydrocarbon distillate. The procedure given in the previous publication includes a wash with alcoholic potassium sulfide solution.

Method B. APPARATUS. No specialized apparatus was required for Method B, the determination being carried out in a modified Babcock bottle (*2*).

REAGENTS. The cooperative work was carried out with ethanol solutions of reagents, but more recent work indicates methanol to be more suitable.

PROCEDURE. In the cooperative work, the following procedure was used in treating the sample after the reaction with nitrogen tetroxide:

Dilute alcoholic sodium hydroxide solution was added with agitation of the bottle, until a light red color of the lower layer was obtained. Next, 11 to 12 ml. of alcoholic potassium sulfide solution were added gradually, and the bottle was stoppered and vigorously shaken for 0.5 minute. After cooling, 11 to 12 ml. of water were added, followed by the addition of sufficient alcohol-water solution (1 to 1) to bring the unreacted portion of test sample into the graduated section of the neck of the bottle. After the bottle was shaken and centrifuged, the volume of unreacted sample was measured (*3*).

COOPERATIVE EVALUATION OF METHODS

Cooperative testing of the nitrogen tetroxide procedures was carried out by nine laboratories, and the results obtained on a set

Table III. Inspections on Base Stock[a] Used in Preparing A.S.T.M. Cooperative Samples B-5 to B-8

Gravity, ° A.P.I.	56.2
A.S.T.M. Distillation, ° F	
I.B.P.	192
5%	222
10%	231
20%	241
30%	250
40%	259
50%	266
60%	274
70%	284
80%	295
90%	310
E.P.	358
Recovery, %	99.0
Residue, %	0.9
Loss, %	0.1
Refractive index, n_D^{20}	1.4194
Density, d^{20}	0.7489
Reid vapor pressure, lb./sq. inch	1.2
Bromine No. (ES-45a)	0.1
Specific dispersion	108.0
Total acid absorption, vol. % (ES-45a)	11.5
Sulfur, wt. %	0.009

[a] Oklahoma City straight-run naphtha.

Table IV. Summary of Determination of Olefin Content of A.S.T.M. Cooperative Samples by Nitrogen Tetroxide Methods

Laboratory	Volume % Olefins[a] Method A Product receiver 1	Volume % Olefins[a] Method A Product receiver 2	Method B	Deviation from Average Method A Product receiver 1	Deviation from Average Method A Product receiver 2	Method B	Deviation from Volume % Olefins Blended Method A Product receiver 1	Deviation from Volume % Olefins Blended Method A Product receiver 2	Method B
				Sample B-5					
A	12.4	11.4	12.0	0.8	0.8	0.5	1.5	0.5	1.1
B	11.1	..	11.8	0.5	..	0.7	0.2	..	0.9
C	11.3	12.2	11.5	0.3	0.0	1.0	0.4	1.3	0.6
D	13.2	13.8	12.0	1.6	1.6	0.5	2.3	2.9	1.1
E	11.0	12.5	13.0	0.6	0.3	0.5	0.1	1.6	2.1
F	11.2	11.2	12.0	0.4	1.0	0.5	0.3	0.3	1.1
G	11.9	12.4	14.0	0.3	0.2	1.5	1.0	1.5	3.1
H	10.8	10.2	11.3	0.8	2.0	1.2	0.1	0.7	0.4
I	15.3[b]	13.7	15.0	3.7[b]	1.5	2.5	4.4[b]	2.8	4.1
Av.	(11.6)	(12.2)	(12.5)	(0.7)	(0.9)	(1.0)	(0.7)	(1.5)	(1.6)
				Sample B-6					
A	21.3	20.0	20.0	1.5	0.4	0.3	2.3	1.0	1.0
B	19.6	..	20.0	0.2	..	0.3	0.6	..	1.0
C	20.4	19.7	21.5	0.6	0.1	1.2	1.4	0.7	2.5
D	19.4	19.6	19.5	0.4	0.0	0.8	0.4	0.6	0.5
E	19.9	19.7	19.5	0.1	0.1	0.8	0.9	0.7	0.5
F	19.3	19.1	19.5	0.5	0.5	0.8	0.3	0.1	0.5
G	19.0	31.2[b]	22.0	0.8	11.6[b]	1.7	0.0	12.2[b]	3.0
H	18.9	19.1	19.3	0.9	0.5	1.0	0.1	0.1	0.3
I	20.5	19.7	21.5	0.7	0.1	1.2	1.5	0.7	2.5
Av.	(19.8)	(19.6)	(20.3)	(0.8)	(0.2)	(0.9)	(0.8)	(0.6)	(1.3)
				Sample B-7					
A	30.0	31.2	30.7	0.8	1.4	0.8	1.0	2.2	1.
B	29.9	..	30.4	0.7	..	0.5	0.9	..	1.4
C	30.0	29.6	31.0	0.8	0.2	1.1	1.0	0.6	2.0
D	29.0	29.2	28.8	0.2	0.6	1.1	0.0	0.2	0.2
E	27.0	28.7	30.1	2.2	1.1	0.2	2.0	0.3	1.1
F	29.1	29.3	29.5	0.1	0.5	0.4	0.1	0.3	0.5
G	27.0	31.0	28.0	2.2	1.2	1.9	2.0	2.0	1.0
H	28.6	30.2	29.0	0.6	0.4	0.9	0.4	1.2	0.0
I	32.2	29.5	32.0	2.0	0.3	2.1	3.2	0.5	3.0
Av.	(29.2)	(29.8)	(29.9)	(1.1)	(0.7)	(1.0)	(1.2)	(0.9)	(1.2)
				Sample B-8					
A	16.9	18.3	16.0	0.9	2.1	0.0	1.1	0.3	2.0
B	16.3	..	14.5	0.3	..	1.5	1.7	..	3.5
C	17.6	17.5	17.0	1.6	1.3	1.0	0.4	0.5	1.0
D	14.8	15.5	15.0	1.2	0.7	1.0	3.2	2.5	3.0
E	14.8	15.3	16.5	1.2	0.9	0.5	3.2	2.7	1.5
F	15.4	15.5	15.0	0.6	0.7	1.0	2.6	2.5	3.0
G	9.7[b]	15.4	16.0	6.3[b]	0.8	0.0	8.3[b]	2.6	2.0
H	14.5	15.0	15.0	1.5	1.2	1.0	3.5	3.0	3.0
I	18.0	17.3	19.0	2.0	1.1	3.0	0.0	0.7	1.0
Av.	(16.0)	(16.2)	(16.0)	(1.2)	(1.1)	(1.0)	(2.0)	(1.9)	(2.2)

[a] Volume % olefins listed are averages reported from each laboratory.
[b] Not included in averages.

Table V. Summary of Standard Deviations Found in Determinations of Olefin Content of Cooperative Samples B-5 to B-8 by Nitrogen Tetroxide Methods

Sample	Olefins, Volume %: Blended	Olefins, Volume % Average Found[a]: Method A, Product receiver 1	Olefins, Volume % Average Found[a]: Method A, Product receiver 2	Olefins, Volume % Average Found[a]: Method B	Standard Deviation, From Blended: Method A, Product receiver 1	Standard Deviation, From Blended: Method A, Product receiver 2	Standard Deviation, From Blended: Method B	Standard Deviation, From Av. Found: Method A, Product receiver 1	Standard Deviation, From Av. Found: Method A, Product receiver 2	Standard Deviation, From Av. Found: Method B	No. of Determinations: Method A, Product receiver 1	No. of Determinations: Method A, Product receiver 2	No. of Determinations: Method B
B-5	10.9	11.6	12.2	12.3	1.2	1.8	1.8	1.0	1.3	1.2	16	15	21
B-6	19.0	19.8	19.6	20.3	1.3	0.7	1.6	1.1	0.5	1.0	17	14	21
B-7	29.0	28.9	30.0	30.0	1.3	1.5	1.7	1.4	1.1	1.2	17	17	27
B-8	18.0	16.0	16.2	15.9	2.4	2.2	2.5	1.4	1.3	1.4	15	16	21
All samples	..	..	..	..	1.6	1.7	1.9	1.2	1.0	1.2	65	62	90
B-5 to B-7, inclusive	..	..	..	..	1.3	1.4	1.7	1.1	1.0	1.1	50	46	69

[a] Averages based on individual determinations.

of synthetic mixtures of olefins are reviewed herein, as offering the best indication of the precision and accuracy of the method as developed and standardized at the present time.

Data on the composition of the test samples, designated B-5 to B-8, are given in Table I, and the properties of the olefins and the base stock used in preparation of the samples are given in Tables II and III, respectively. In general, the samples were made up to contain the following types of olefins:

Sample No.	Types of Olefins
B-5	Normal olefins
B-6	Normal, cyclic, and aromatic olefins and a diolefin
B-7	Normal, cyclic, and aromatic olefins and a diolefin
B-8	Highly branched olefins

While the purity of the olefins used has not been definitely established, the data in Table II show that the properties of the olefins (with the exception of hexene-3) are in fairly good agreement with the literature values (*1*, *4*).

A summary of the results obtained for total olefin content by the nitrogen tetroxide methods is given in Table IV.

DISCUSSION

A statistical analysis of the data obtained in this evaluation of the nitrogen tetroxide methods for olefins gave the following standard deviations:

	Standard Deviation (Based on Total Sample): From % olefin blended	Standard Deviation (Based on Total Sample): From av. % olefin found
Method A (product receiver Type 1)		
All samples	1.6	1.2
B-5 to B-7, inclusive	1.3	1.1
B-8	2.4	1.4
Method B		
All samples	1.9	1.2
B-5 to B-7, inclusive	1.7	1.1
B-8	2.5	1.4

Comparable data on these samples by a bromine titration procedure (A.S.T.M. ES-45a, *2*) show a standard deviation of 1.1 based on the average of all determinations of bromine number. This value is of the same order of magnitude as that indicated by the nitrogen tetroxide procedure. Inasmuch as the bromine number procedure requires an estimation of the molecular weight and specific gravity of olefins present in the mixture to convert to volume per cent olefins, the direct volumetric determination of olefins by the nitrogen tetroxide procedure is considered fundamentally more reliable.

The above data show that Method B compares favorably with Method A, and because of its relative simplicity and rapidity, use of Method B is indicated in cases where only the volume per cent olefins is required.

As indicated by the deviations shown for sample B-8, both procedures give poorer results on highly branched olefins than on mixtures of other types of olefins. In general, the highly branched olefins are more difficult to react completely with nitrogen tetroxide, and the nitrosate reaction products formed are less readily separated from the unreacted hydrocarbons than is the case with other types of olefins.

A summary of the deviations found on each of the samples cooperatively tested is given in Table V. With regard to Method A, the data in this table show no marked difference in precision of results obtained with the two types of product receivers tested.

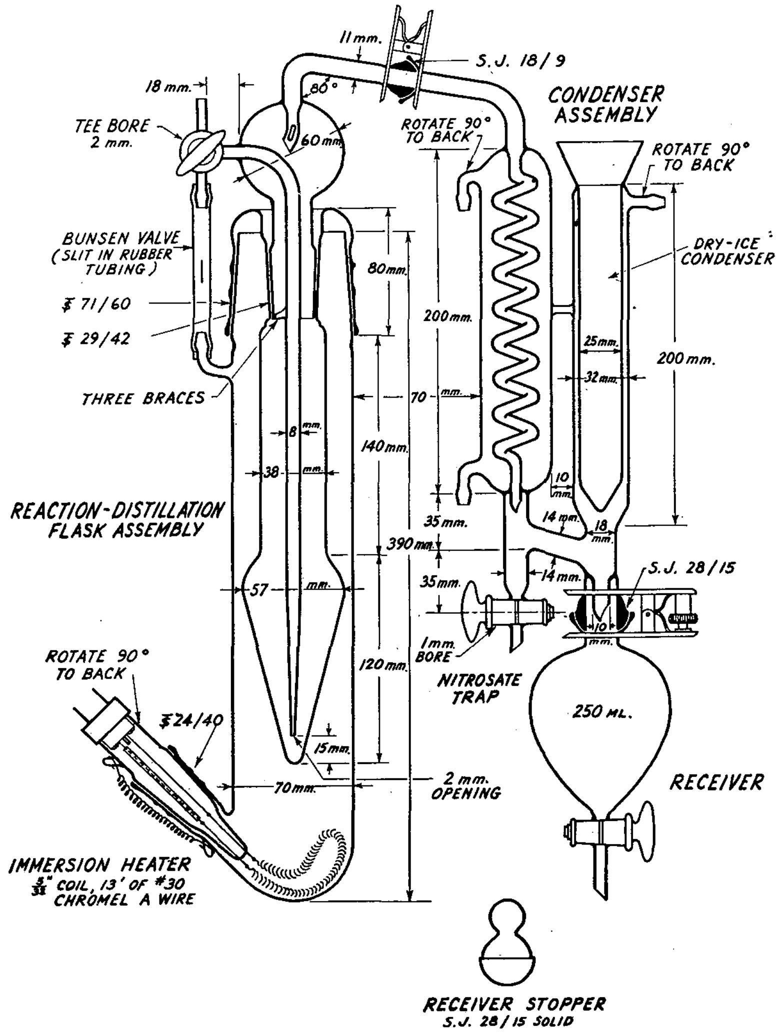

Figure 5. Apparatus for Nitrogen Tetroxide Method of Olefin Determination

Table VI. Comparison of Properties of Unreacted Portion of Test Sample Obtained by Nitrogen Tetroxide Method A with Properties of Base Stock Used in Test Samples

	Product Receiver Type 1				Product Receiver Type 2			
Lab.	Density, d^{20}	Refractive index, n_D^{20}	Bromine No. by method ES-45a	Acid absorption by method ES-45a, vol. %	Density, d^{20}	Refractive index, n_D^{20}	Bromine No. by method ES-45a	Acid absorption by method ES-45a, vol. %
				Straight-Run Base Stock				
	0.7489	1.4194	0.1	11.5	0.7489	1.4194	0.1	11.5
				Sample B-5				
A	0.7510	1.4198	0.0	10.5	0.7504	1.4194	0.0	9.0
B	0.7485	1.4184	0.2	11.0	....	....	..	..
C	0.7503	1.4197	0.05	11.4	0.7512	1.4201	0.05	12.5
D	0.7504	1.4196	0.1	11.2	0.7512	1.4201	0.1	11.4
E	0.7509	1.4198	0.5	11.5	....	....	..	..
F	0.7485	1.4196	0.0	12.0	0.7481	1.4196	0.0	12.0
G	0.7526	1.4202	0.23	11.3	0.7522	1.4203	0.13	12.5
H	0.7507	1.4199	..	..	0.7507	1.4199	..	..
I	0.7503	1.4202	0.3	11.0	0.7506	1.4204	0.3	10.5
Av.	(0.7504)	(1.4197)	(0.17)	(11.2)	(0.7506)	(1.4200)	(0.10)	(11.3)
				Sample B-6				
A	0.7502	1.4198	0.0	10.0	0.7508	1.4193	0.0	11.0
B	0.7485	1.4189	0.1	11.0	....	....	..	..
C	0.7505	1.4197	0.05	12.3	0.7511	1.4200	0.08	12.3
D	0.7507	1.4196	0.1	11.7	0.7506	1.4196	0.1	11.2
E	......	......	...	..	0.7525	1.4206	0.5	11.0
F	0.7481	1.4196	0.0	12.0	0.7489	1.4197	0.0	11.0
G	0.7545	1.4204	0.18	12.2	0.7508	1.4195	0.14	10.8
H	0.7513	1.4199	..	..	0.7506	1.4199	..	..
I	0.7501	1.4202	0.3	11.0	0.7505	1.4203	0.3	11.5
Av.	(0.7505)	(1.4198)	(0.10)	(11.5)	(0.7507)	(1.4199)	(0.16)	(11.3)
				Sample B-7				
A	0.7506	1.4199	0.0	10.5	0.7514	1.4201	0.0	11.5
B	0.7485	1.4177	0.1	10.0	....	....	..	..
C	0.7505	1.4195	0.10	12.0	0.7517	1.4202	0.08	12.8
D	0.7499	1.4191	0.7	11.2	0.7509	1.4194	0.2	11.2
E	0.7529	1.4203	0.5	12.0	....	....	..	..
F	0.7491	1.4197	0.0	12.5	0.7493	1.4198	0.0	12.0
G	0.7619[a]	1.4214	0.09	16.3[a]	0.7518	1.4195	0.06	11.3
H	0.7510	1.4198	..	..	0.7509	1.4202	..	..
I	0.7500	1.4198	0.3	10.0	0.7512	1.4203	0.3	11.0
Av.	(0.7503)	(1.4197)	(0.22)	(11.2)	(0.7510)	(1.4199)	(0.11)	(11.6)
				Sample B-8				
A	0.7528	1.4194	0.2	12.0	0.7523	1.4199	0.1	9.5
B	0.7486	1.4183	0.6	10.5	....	....	..	..
C	0.7514	1.4197	0.18	12.8	0.7538	1.4198	0.10	13.5
D	0.7513	1.4192	1.4	13.2	0.7535	1.4194	1.3	13.2
E	0.7557	1.4195	0.5	12.5	....	....	..	..
F	0.7505	1.4195	1.0	14.0	0.7505	1.4196	1.7	14.0
G	0.7680[a]	1.4220	0.46	20.1[a]	0.7583	1.4203	0.15	14.3
H	0.7559	1.4200	..	..	0.7564	1.4200	..	..
I	0.7552	1.4204	0.3	13.5	0.7513	1.4202	0.3	12.0
Av.	(0.7527)	(1.4198)	(0.58)	(12.6)	(0.7537)	(1.4200)	(0.61)	(12.8)

[a] Not included in averages.

The average values for handling loss, as obtained by "blank" determinations on the samples, were 0.45 ml. with product receiver Type 1 and 0.55 ml. with product receiver Type 2. The Type 1 receiver is preferred for the more volatile samples.

Since the same straight-run base stock was used in the four synthetic mixtures used in the investigation, the properties of the "unreacted portion" of test sample obtained by Method A can be compared with those of the base stock to indicate completeness of olefin removal and absence of undesirable side reactions. This comparison is shown in Table VI, which gives the average of determined properties such as density, refractive index, bromine number, and acid absorption on the unreacted portions of samples B-5 to B-8. Except in the case of sample B-8, these properties are fairly close to those of the original base stock, indicating practically complete removal of olefins without substantial change in the other hydrocarbon types. Density and nitrogen determinations, however, indicate nitrogen tetroxide reaction products, in amounts of the order of 0.05 to 0.25% by weight, remaining in the unreacted portion.

Since the reaction of olefins with nitrogen tetroxide is carried out in a temperature range of 80° to 100° F., the procedures given are limited to mixtures containing hexanes or higher boiling hydrocarbons, and therefore should find application in analysis of depentanized gasolines. It is probable that suitable modifications of apparatus and procedure can be developed to handle samples containing appreciable amounts of pentanes and lighter hydrocarbons.

A recent design of apparatus for Method A, submitted by the Shell Development Company laboratory, is shown in Figure 5. While this apparatus has not been cooperatively tested, it has been used by several laboratories and appears to have certain advantages, such as saving in laboratory space and in time required to make a determination.

Two possible hazards exist in the handling of nitrogen tetroxide in combination with olefins—namely, the degree of stability of the reaction products and the toxicity of nitrogen tetroxide. While several references have been made to the fact that reaction products of light olefins and diolefins with nitrogen tetroxide are unstable, an investigation of the products from representative samples, such as thermal and catalytic gasoline and pentenes, show them to be nonexplosive, even by the use of detonators (*6*). However, olefin–nitrogen tetroxide compounds are thermally unstable and subject to rapid decomposition if heated directly much above 250° to 300° F. Violent reactions have occurred where nitrogen tetroxide has been left in contact with hydrocarbons for long periods of time. The presence of oil in pipes, valves, etc., used for nitrogen tetroxide should be avoided.

The nitrogen tetroxide reaction should be carried out under a hood, and observance of safe laboratory practice in handling toxic gases is recommended (*5*).

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DETERMINATION OF ORGANIC PEROXIDES

Evaluation of a Modified Iodometric Method

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An iodometric method for peroxide determination has been modified and extensively tested. The modified method accurately determines peroxides present in autoxidized olefins but, in common with all other methods, it gives only empirical results when applied to peroxides formed in conjugated diolefins. Experiments proved that under the conditions of the method iodine does not add to mono-olefins, and that in the absence of peroxides it does not add to conjugated diolefins. The method has been found more accurate and more widely applicable than iodometric methods employing acetic acid as solvent.

IODOMETRIC methods as well as ferrous ion methods have been widely used for the determination of peroxides in oxidized organic materials. Most of the proposed iodometric methods involve reduction of peroxides by iodide ion in acetic acid solution with or without addition of a strong mineral acid. The well-known procedures of Wheeler (*16*), Lea (*7*), Marks and Morrell (*11*), Franke and Jerchel (*3*), Liebhafsky and Sharkey (*8*), Taffel and Revis (*15*), Stansby (*14*), and French, Olcott, and Mattill (*4*) are examples of such methods, some of which use chloroform or carbon tetrachloride to aid in dissolving the sample. Kokatnur and Jelling (*6*) proposed a procedure employing isopropyl alcohol as solvent, in conjunction with a small amount of acetic acid and potassium iodide. Nozaki (*12*) has recently reported a procedure in which acetic anhydride is used as the solvent.

Many differences of opinion exist concerning the reliability of iodometric methods. It has been well established that many peroxycarboxylic acids, diacyl peroxides, hydroperoxides, and other peroxide compounds can be determined quantitatively by iodometric methods, although a few reports exist doubting the accuracy of certain iodometric methods on such simple peroxides as cyclohexene and Tetralin peroxides. The most common criticism has been that iodine liberated in the reaction disappears by addition to olefinic double bonds; this assertion has been based upon dependence of results on sample size with certain materials and upon test experiments involving reaction of free iodine rather than triiodide ion. Wheeler (*16*) found that when iodide ion was present iodine did not add to certain unsaturated peroxide-free oils, but proof was lacking that triiodide did not react with olefins in the presence of peroxides. Panyutin and Gindin (*13*) formulated a procedure by which they measured iodide added, iodine found, and iodide unoxidized, thus hoping to compensate for iodine addition, but the procedure itself was so different from the usual procedures that information presented in that report did not prove or disprove iodine addition under normal conditions of iodometric methods.

Another criticism which might be directed at iodometric methods, particularly those employing strong acid, is the possibility of reduction of organic compounds other than peroxides, including possible reduction of any alkylene diiodides formed by addition of iodine to olefin. Atmospheric oxygen is known to cause high results with most iodometric methods, particularly in the presence of strong acids, and methods employing sodium bicarbonate or solid carbon dioxide (*1*, *8*) were designed to overcome this defect. The Kokatnur-Jelling method (*6*) was reported not to be influenced by atmospheric oxygen.

For general use the method proposed by Kokatnur and Jelling (*6*) has been found the most suitable of the iodometric methods tested. [Since this work was completed, Nozaki (*12*) has reported that use of acetic anhydride in place of acetic acid overcomes the disadvantages inherent in the use of the latter as solvent.] Modifications found advantageous are: (1) replacement of potassium iodide by sodium iodide which is much more soluble in the reaction mixture and makes possible a higher concentration of iodide, tending to increase the reaction rate and to decrease possible addition of iodine to unsaturated materials; and (2) elimination of water from the reaction mixture to avoid the low results obtained on autoxidized diolefins in the presence of water. [Lips, Chapman, and McFarlane (*9*) noted that presence of water markedly decreased results obtained on fats by an iodometric method, and Liebhafsky and Sharkey (*8*) observed that water retards peroxide reduction by iodide.] In order to avoid possible interference by oxygen in the experimental work, the reaction mixture was kept under a blanket of carbon dioxide, and sample and reaction mixture were deaerated prior to analysis; however, such precautions have been found unnecessary for general use.

Experiments using the modified iodide method show that results on known hydroperoxides are accurate, since wide variation in reaction conditions produces little change in results which are already close to theoretical. The fact that peroxide was not volatilized by passage of carbon dioxide gas was proved by tests using *tert*-butyl hydroperoxide. It was found that appreciable amounts of water must be present in the mixture at the titration end point in order to avoid high results due to the slowness of reaction between iodine and thiosulfate and consequent overtitration, especially when the titer is small. This effect had been noted by Liebhafsky and Sharkey (*8*) while studying a method utilizing acetic acid as solvent.

Variation in reaction conditions produced little change in results on materials containing no autoxidized conjugated diolefins, indicating that the method is accurate when applied to such materials; this is consistent with recent observations that mono-olefin peroxides and initially formed ether peroxides are, in fact, hydroperoxides. However, results on diolefins and ascaridole showed wide variation with changes in reaction conditions, indicating that such bridge-type peroxides are not determined accurately by this method.

Experiments have demonstrated that under the conditions of the method iodine does not add to mono-olefins and that, in the absence of peroxides, it does not add to diolefins. One experiment indicated that iodine might be absorbed by diolefins in the presence of diolefin peroxides. The sodium iodide–isopropyl alcohol method was found to be as useful in all cases as sodium iodide–acetic acid methods and to have the advantages of somewhat more general applicability and comparative freedom from interference by atmospheric oxygen.

EXPERIMENTAL ANALYTICAL PROCEDURE

Into a 250-ml. Erlenmeyer flask equipped with a gas inlet tube introduce 40 ml. of dry isopropyl alcohol, 2 ml. of glacial acetic acid, and up to 10 ml. (usually 5 ml.) of the sample, containing up to 2 milliequivalents of peroxides. Connect the flask to a

Table I. Effect of Absence of Water on Accuracy of Iodometric Titration

Volume of Standard Iodine Solution	Calculated Titer, 0.1 *N* $Na_2S_2O_3$	Titer Found, 0.1 *N* $Na_2S_2O_3$ Anhydrous	Titer Found, 0.1 *N* $Na_2S_2O_3$ 5 ml. of H_2O added
Ml.	*Ml.*	*Ml.*	*Ml.*
50	11.53	11.57	11.56
25	5.77	5.75	5.78
10	2.31	2.81	2.37
2	0.46	1.02	0.51

Table II. Effect of Manipulative Variables in the Sodium Iodide–Isopropyl Alcohol Method on Results for Known Peroxides[a]

	Tetralin Peroxide, %[b]		*tert*-Butyl Hydroperoxide, %[b]		Hydrogen Peroxide, %[b]	Benzoyl Peroxide, %[b]		Ascaridole, %[b]
Variable	Anhydrous	5 ml. of H_2O before titration	Anhydrous	5 ml. of H_2O before titration	5 ml. of H_2O before titration	Anhydrous	5 ml. of H_2O before titration	Anhydrous
Reaction time								
2 min.	103.7	97.3	96.7	96.5	29.7	100.2	98.8	7.3
5 min.	105.1	97.1	96.5	96.5	29.6	100.2	98.0	11.2
15 min.	102.4	97.3	95.8	96.0	29.4	100.7	98.5	25.7
Sample size								
2 ml.	105.7	96.2	103.7	95.1	29.9	104.0	98.3	55.6
5 ml.	102.4	97.3	95.8	96.0	29.4	100.7	98.1	25.7
10 ml.	96.7	97.2	96.2	96.2	..	...	...	..
Amount of iodide[c]								
2 grams	102.2	96.9	..	96.3	29.4	99.4	98.8	25.1
7 grams	99.4	98.1	..	97.5	29.7	102.3	100.2	28.6
Effect of 5 ml. of H_2O								
Added at start	97.2		96.0		..	100.7		3.7
Added after reflux	97.0		96.0		..	98.5		18.4
No H_2O	102.4		95.8		..	98.5		25.7
Effect of heat								
30-min. reflux before I^- added	97.4	93.5	..	94.2	29.0	84.3	86.2	23.5
0-min. reflux before I^- added	102.4	97.3	95.8	96.0	29.4	100.7	98.5	25.7

[a] Dissolved in benzene (C.P. thiophene-free), about 0.1 *N* except hydrogen peroxide, which was diluted with water.

[b] Per cent recovery based on 100% purity. "Anhydrous" refers to anhydrous conditions of experimental method. Other columns of data obtained by adding 5 ml. of water to reaction mixture just before titration.

[c] Method modified: sodium iodide dissolved by refluxing in isopropyl alcohol–acetic acid, followed by heating to reflux, and addition of sample through condenser. Carbon dioxide used in usual way before and after refluxing.

reflux condenser and pass carbon dioxide gas through the mixture for 3 minutes. Stop the carbon dioxide flow, heat the solution to reflux, add through the condenser 10 ml. of isopropyl alcohol saturated with sodium iodide, and heat the mixture at gentle reflux for 15 ± 0.5 minutes. Resume the carbon dioxide flow, disconnect the flask from the condenser, and titrate the contents immediately with 0.1 *N* sodium thiosulfate to the disappearance of the yellow color (use 0.01 *N* thiosulfate for very low peroxide concentrations).

EXPERIMENTAL

Materials Used. Tetrahydronaphthyl hydroperoxide (Tetralin peroxide) was prepared by air oxidation of Tetralin at 75°, crystallization, and recrystallization. α,α-Dimethylbenzyl hydroperoxide (cumene peroxide) was prepared from cumene by a method similar to that of Hock and Lang (*5*). Hydrogen peroxide was a sample of Baker's C.P. 30% (in water), assaying 29.9%. *tert*-Butyl hydroperoxide was prepared by careful distillation of Union Bay State material, and analyzed close to 96.5% by the procedure given above. Benzoyl peroxide was obtained from Lucidol Corporation. Ascaridole, obtained from Eastman Kodak Company, was said to be better than 99% pure, and analyzed 72.3% carbon, 9.8% hydrogen (theory 71.4% carbon, 9.6% hydrogen).

The following materials were autoxidized by allowing them to stand under oxygen in diffused daylight until analysis indicated a reasonably high peroxide content (air was used in the case of 2-pentene): Diisobutylene, consisting of about 75% of 2,2,4-trimethyl-1-pentene and 25% of other isomeric octenes, was not redistilled before autoxidation. 2-Pentene, prepared by dehydration of *sec*-amyl alcohol, was carefully distilled. The product probably contained a small amount of 1-pentene. Cyclohexene, Eastman Kodak Company material, was dried over potassium carbonate and potassium hydroxide and redistilled, the fraction distilling between 83.0° and 83.3° being retained. Tetralin, also obtained from Eastman Kodak Company (practical grade), was redistilled, the fraction boiling between 204.3° and 207.3° being retained. Methylpentadiene, prepared by dehydration of 2-methyl-2,4-dihydroxypentane, was carefully distilled before allowing it to autoxidize. It consisted of about 70% 2-methyl-1,3-pentadiene and 30% 4-methyl-1,3-pentadiene. Isoprene, redistilled, was 97.1% pure (determined by freezing point). Diethyl ether was anhydrous Merck reagent.

Effect of Water on the Titration. It was found that the reaction between sodium thiosulfate and triiodide ion is rather slow unless 5 to 10% of water is present in the reaction mixture. When the titration volume is reasonably large, sufficient water is furnished by the thiosulfate solution but with low titers water must be added before titration. This effect is shown in Table I, which summarizes experiments in which known amounts of a standard isopropyl alcohol solution of iodine contained in the reaction mixture were titrated hot, using a constant total amount of reaction mixture [*x* ml. of standard solution iodine in isopropyl alcohol, (50 − *x*) ml. of isopropyl alcohol, 2 ml. of glacial acetic acid, and 2 grams of sodium iodide].

Accuracy of Method and Effect of Manipulative Variables on Results. The known peroxides were tested to study the effect of variations in heating time, reaction time, sample size, amount of iodine, and amount of water (Table II). These tests indicate that (1) the amount of iodide is not critical, provided a large excess is present, (2) reaction time and sample size are not critical for the peroxides tested (except for ascaridole, which reduces slowly), (3) only the ascaridole analysis was markedly affected by the presence of water during the reaction, and (4) except for benzoyl peroxide the peroxides are stable toward heat. Consistent results close to theoretical with the hydroperoxides indicate that the method is accurate for their determination. Additional support for this conclusion is given by consistent results of 94% obtained on a sample of α,α-dimethylbenzyl hydroperoxide prepared by autoxidation.

The experimental procedure was applied with variations to the autoxidized materials, with results shown in Table III. With materials containing no conjugated diolefins, results were affected little by changes in the experimental conditions, whereas results with autoxidized isoprene and methylpentadiene were critically dependent on the conditions employed. The diolefin peroxides react slowly and incompletely, like ascaridole, and results showing dependence on sample size and amount of iodide ion demonstrate that the rate of reduction depends on the concentration of iodide ion in the mixture rather than on the concentration of the peroxides. Water present during the reflux period causes lower values to be obtained in some cases, and to prevent this effect the exclusion of water during the reflux period is recommended.

The results demonstrate conclusively that peroxides in autoxidized conjugated diolefins differ radically from those in other materials; the latter are now generally accepted to be hydroperoxides, whereas Bodendorff (*2*) has demonstrated that conjugated diolefins form peroxides largely by 1,4 addition to produce intramolecular peroxides of the ascaridole type, or polymeric

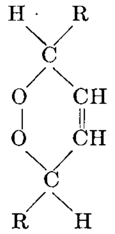
Table III. Effect of Manipulative Variables in the Sodium Iodide–Isopropyl Alcohol Method on Peroxide Numbers of Autoxidized Materials

Variable	Peroxide Number, Milliequivalents per Liter Diiso-butylene	2-Pentane	Cyclo-hexene	Tetralin	Diethyl ether	Methyl-pentadiene	Iso-prene
Reaction time							
2 min.	11.0	40.0	83.6	114	12.0	22	31
5 min.	11.8	40.2	86.7	115	12.1	33	52
15 min.	11.6	40.4	85.0	113	12.0	61	92
Sample size[a]							
2 ml.	. .	. .	. .	112	11.7	99	88
4 ml.	11.6	42.6	85.0	. .	. .	. .	. .
5 ml.	. .	. .	. .	109	12.0	55	48
10 ml.	9.8	38.3	83.3	. .	12.0	. .	. .
Amount of iodide[b]							
2 grams	11.2	44.8	84.9	117	12.1	67	94
7 grams	11.8	42.4	84.9	118	12.6	227	128
Effect of 5 ml. of H_2O							
Added at start	8.6	38.8	82.3	113	11.9	19	15
Added after reflux	9.2	39.6	82.6	113	12.1	57	78
No H_2O	11.6	40.4	85.0	113	11.7	61	92
Effect of heat							
30-min. reflux before I^- added	12.6	39.8	81.6	109	11.8	59	82
No reflux before I^- added	11.6	40.4	85.0	113	12.1	61	92

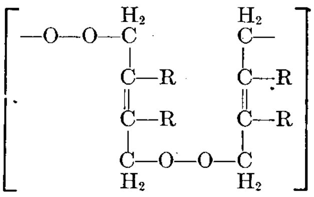
[a] Except in case of conjugated dienes, indicated variation of results with sample size can be ascribed chiefly to fact that no water was added before titration.

[b] Method modified, see c, Table II.

peroxides by intermolecular peroxy-bridging to the 1- or 4-positions of other molecules:



Intramolecular peroxide from conjugated diolefin



Intermolecular polymeric peroxide from conjugated diolefin

Such peroxides would be expected to react differently from the simple alkenyl hydroperoxides which are formed with mono-olefins by oxidative attack at the carbon atom alpha to a double bond. The fact that ascaridole reacts in a way very similar to the autoxidized diolefins is to be expected in view of Bodendorff's observations that the monomeric product formed from the autoxidation of the conjugated diolefin, 1,3-menthadiene, is chemically and structurally similar to ascaridole. In addition to these observations and the fact that the hydroperoxides react very rapidly with iodide ion, another point to be noted is the stability of all of the peroxides in autoxidized materials. In no case did a significantly decreased final value result from refluxing the sample in the reaction mixture for 30 minutes before addition of iodide ion. Any slight decreases obtained may possibly be due to reduction of the peroxide by the alcohol.

INTERFERENCES

Iodine Absorption by Unsaturated Materials. To test the magnitude of this potential source of error, samples of isoprene and cyclohexene were fractionally distilled into a receiver through which oxygen-free nitrogen was slowly passed. Ten-milliliter portions of each of these peroxide-free materials were subjected to two modifications of the prescribed procedure. In one, 10 ml. of isopropyl alcohol containing about 0.2 milliequivalent of iodine were added following the addition of the iodide, and in the other the iodine solution was substituted for the iodide solution. In another set of experiments, 5 ml. of water were added to the mixture at the start. Results, shown in Table IV, demonstrate that in the absence of iodide ion a considerable fraction of the iodine is lost, particularly in the presence of water. This is in agreement with observations by Margosches, Hinner, and Friedmann (*10*) on the effect of water on rate of iodine addition to unsaturated materials. When iodine is combined with iodide in the form of triiodide ion, no evidence of loss is observed (with peroxide-free material).

Inasmuch as the amount of iodine lost is approximately proportional to the amount originally present, the fact that no loss occurred in the presence of iodide is undoubtedly due to the formation of unreactive triiodide ion and resultant small concentration of free iodine.

In order to determine whether a peroxide such as benzoyl peroxide could catalyze addition of iodine as triiodide to olefins, a weighed quantity of sodium iodide was dissolved by refluxing in 40 ml. of isopropyl alcohol and 2 ml. of acetic acid in the presence of carbon dioxide. Five milliliters of water were added in some cases. Five milliliters of purified isoprene and 10 ml. of a standard benzoyl peroxide solution in benzene were then added, and the mixture was refluxed 15 minutes and titrated, maintaining a blanket of carbon dioxide at all times. Results are tabulated in Table V. No peroxide-catalyzed addition of iodine is observed.

Nevertheless, definite evidence was still lacking as to whether iodine as triiodide is absorbed by diolefins in the presence of diolefin peroxides. To test this point, a 1-ml. sample of autoxidized methylpentadiene was subjected to analysis in the usual fashion in the presence of (1) 4 ml. of freshly distilled peroxide-free methylpentadiene and (2) 4 ml. of benzene. Results of 0.309 and 0.341 milliequivalent, respectively, were obtained, which may indicate some absorption of iodine in the presence of the diolefin peroxide (lower results with greater concentration of diolefin).

Possibility of Reduction of Olefins or Alkylene Diiodides during Analysis. If hydrogen iodide should add to olefins to produce alkyl iodides, or if iodine should add to produce alkylene diiodides, reduction of such organic iodides by hydrogen iodide would produce iodine and lead to high results. In order to test whether this is at all likely, the method was applied to 1 ml. of autoxidized methylpentadiene both with and without the addition of 2 ml. of pure ethyl iodide. Titers were 16.3 ± 0.2 ml. of 0.01 *N* thiosulfate, indicating that in the presence of diolefin peroxides simple alkyl iodides are not reduced by the iodide reagent.

Table IV. Addition of Iodine to Unsaturated Materials under Conditions of Analysis

Material	I_2 or I_3^- Added, Equivalent × 10^3	I_2 or I_3^- Found after Reflux, Equivalent × 10^3 In anhydrous medium	In presence of 5 ml. of H_2O
Isoprene	0.1890 I_2[a]	0.1600	0.1400
	0.0756 I_2[a]	0.0601	0.0432
	0.0378 I_2[a]	0.0249	0.0161
Cyclohexene	0.1760 I_2[a]	0.1519	0.0971
Isoprene	0.2278 I_3^-	0.2274	0.2260
	0.0911 I_3^-	0.0906	0.0907
	0.0456 I_3^-	0.0459	0.0457
Cyclohexene	0.2050 I_3^-	0.2049	0.2050

[a] Determined by refluxing concentrated solutions 15 minutes and titrating. The two dilute solution concentrations were calculated from dilution factors. About 0.02 milliequivalent of iodine was lost from concentrated iodine solutions themselves on refluxing

Interference by Air. A sample of methylpentadiene, analyzed in the prescribed way, gave 2.3 milliequivalents of peroxide per liter. When an air stream was substituted for carbon dioxide, a value of 3.3 milliequivalents per liter was obtained, and instability of the end point was troublesome. Approximately the same absolute difference in results was noted on diolefin samples of higher peroxide content, whereas with cyclohexene and other simple olefins no significant difference was noted. It is concluded that exclusion of air is essential only if the method is used for analyzing diolefin samples of low peroxide content.

PROCEDURE RECOMMENDED FOR GENERAL USE

The following method, which is closely similar to the Kokatnur-Jelling method, is recommended for general use on materials containing no conjugated diolefins:

Into a 250-ml. Erlenmeyer flask introduce 40 ml. of dry isopropyl alcohol, 2 ml. of glacial acetic acid, and the sample (up to 10 ml., ordinarily 5 ml.). Heat to reflux, add 10 ml. of isopropyl alcohol saturated at room temperature with sodium iodide (prepared by refluxing 25 grams of sodium iodide with 100 ml. of isopropyl alcohol), reflux 5 minutes, add 5 ml. of water, and titrate with 0.1 *N* or 0.01 *N* sodium thiosulfate. Blank determinations on the reagents will be nil unless oxidizing impurities are present in the isopropyl alcohol; therefore a blank determination on each new batch of alcohol is sufficient.

Although the method is not recommended for use on conjugated diolefins, it is sometimes useful for obtaining precise empirical results, provided an atmosphere of carbon dioxide is maintained in the flask during the analysis.

Table V. Addition of Triiodide Ions to Isoprene in Presence of Benzoyl Peroxide

NaI Present, Grams	Benzoyl Peroxide Added, Eq. × 10^3	I_3^- Found after Reflux, Equivalent × 10^3	
		In anhydrous medium	In presence of water
2	0.871	0.863	0.862
7	0.871	0.877	0.867

COMPARISON WITH METHODS EMPLOYING ACETIC ACID AS SOLVENT

The following two methods, employing acetic acid as solvent, were compared with the recommended method described above.

Acetic Acid Reflux Methods. Into a 250-ml. Erlenmeyer flask equipped with a gas inlet tube introduce 50 ml. of glacial acetic acid and 5 ml. of sample. Connect to a reflux condenser, pass carbon dioxide through the solution slowly for 2 minutes, stop the flow, and heat the mixture to reflux. Add 2 ml. of a saturated aqueous solution of sodium iodide through the condenser, reflux for 15 minutes, start the carbon dioxide flow, add 100 ml. of distilled water, cool the contents to room temperature, and titrate with thiosulfate to the disappearance of the yellow color, maintaining gentle carbon dioxide flow during the titration. Make a blank determination on the reagents in a similar manner.

Acetic Acid Room-Temperature Method. Same as the above, except that after carbon dioxide is passed through the solution for 2 minutes, add the iodide, stop the carbon dioxide flow, stopper the flask, and allow it to stand in the dark for 15 minutes at room temperature before resuming the carbon dioxide flow, diluting with water, and titrating.

Comparative results are shown in Table VI. It is evident that, except for ascaridole, results are generally lower when acetic acid is used, and results by the acetic acid reflux method are ordinarily lower than are those by the acetic acid room temperature method. In the case of the diolefins, the dark-colored polymer which forms, particularly on heating, obscures the end point. The lower results by the method employing heat are due to destruction of peroxides during the period of heating to reflux, as shown by the following experiment: A sample of cyclohexene gave a value of 95.9 milliequivalents per liter by the room-temperature acetic acid method and 85.7 milliequivalents per liter by the acetic acid–reflux method. When the reaction mixture was refluxed without iodide for 15 minutes, cooled rapidly, and then treated according to the room temperature acetic acid method, a value of only 72.2 milliequivalents per liter was obtained. It seems likely that the peroxides are less stable in acetic acid than in isopropyl alcohol.

Table VI. Comparison of Results by Sodium Iodide–Isopropyl Alcohol and Sodium Iodide–Acetic Acid Methods

Material Analyzed[a]	Solvent and Condition: Isopropyl alcohol, reflux	Acetic acid, room temperature	Acetic acid, reflux
	Apparent Peroxide Content, %		
Tetralin peroxide	97.3	96.3	91.1
tert-Butyl hydroperoxide	96.0	96.8	95.7
Hydrogen peroxide (29.9%)	29.4	29.6	29.4
Benzoyl peroxide	99.4	99.4	85.2
Ascaridole	25.7	34.1	71.4
	Peroxide No., Milliequivalents per Liter		
Diisobutylene	36.9[b]	27.5	34.7
2-Pentene	45.9	41.6	40.4
Cyclohexene	95.1[c]	91.8	80.6
Tetralin	126.1	123.8	109.3
Diethyl ether	12.2	21.4	11.3
Methylpentadiene	53.4	(20)[d]	(100)[d]
Isoprene	68.3[c]	(20)[d]	(100)[d]

[a] With known peroxides samples were about 0.1 *N* solutions in benzene, except that hydrogen peroxide was diluted with water. Autoxidized materials were used directly.

[b] Method modified by adding 5 ml. of water before titration.

[c] Application of isopropyl alcohol method at room temperature gave: cyclohexene, 83.4 me./l., isoprene, 5.3 me./l.

[d] Reaction mixture was very dark in color, with much polymer; results are very much in doubt.

It is concluded that acetic acid as solvent offers no advantages over isopropyl alcohol, other than elimination of the reflux operation. Disadvantages are greater interference by air, occasional slight destruction of peroxides, need for great dilution with water before titration, and increased tendency for diolefinic materials to polymerize to dark-colored products. Use of a strong acid in addition to acetic acid would probably accentuate these difficulties.

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Evaluation of the Ferrous Thiocyanate Colorimetric Method

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The colorimetric ferrous thiocyanate method, first proposed by Young, Vogt, and Nieuwland, has been tested on a variety of autoxidized materials. It was found fundamentally accurate on hydrocarbon materials containing no conjugated diolefins; on diolefins the results varied considerably with time and were therefore of only empirical value. The precision was relatively poor (approximately ± 5 to 10% of the absolute value) but the method was sensitive to very small peroxide concentrations. Presence of high polymer sometimes caused interference because of insolubility and turbidity. The effect of molecular oxygen on the results, first reported by Lea, has been verified. Contrary to Lea's conclusion that the molecular oxygen oxidizes ferrous ion in the presence of peroxide, the presence of dissolved oxygen is necessary to obtain quantitative peroxide results and the absence of oxygen gives very low results. No definite evidence of abnormally high results was found in these investigations.

FERROUS ion has been used extensively as a reducing agent for the determination of organic peroxides. One of the common methods involving ferrous ion, originally proposed by Young, Vogt, and Nieuwland (*7*), comprises reduction of the sample in an acidified solution of ferrous thiocyanate in methanol followed by measurement of the depth of color of the ferric thiocyanate produced. Bolland, Sundralingam, Sutton, and Tristram (*2*) used this method with slight variations in rubber research, and Farmer *et al.* (*3*) based theoretical conclusions on results using this method. Lips, Chapman, and McFarlane (*5*) used a similar method with acetone as solvent in place of methanol.

Young, Vogt, and Nieuwland (*7*) based their claim for accuracy of the method on determinations of pure succinyl peroxide. Bolland *et al.* (*2*) obtained analyses close to theoretical on succinyl peroxide, dihydroxyheptyl peroxide, and cyclohexene peroxide. However, Lea (*4*), using a method similar to that of Lips, Chapman, and McFarlane (*5*), discovered that when air was carefully removed from both sample and reagent the results were only 10 to 30% of those obtained without such treatment; he concluded that atmospheric oxygen and dissolved oxygen were oxidizing ferrous ion in the presence of peroxide (although little atmospheric oxidation takes place in the absence of peroxide) and, therefore, that the results included very large positive errors.

In view of the conflicting reports of accurate values on known peroxides on the one hand and oxidation by air to produce high results on the other hand, experiments were undertaken in order to resolve these differences. By using the method of Bolland, Sundralingam, Sutton, and Tristram, essentially accurate results were obtained on pure *tert*-butyl hydroperoxide, α,α-dimethylbenzyl hydroperoxide (cumene peroxide), and tetrahydronaphthyl hydroperoxide (tetralin peroxide). With autoxidized mono-olefins good agreement was obtained between results by the sodium iodide–isopropyl alcohol and colorimetric methods. However, in all colorimetric analyses wherein oxygen was carefully excluded, the observations of Lea (*4*) were substantiated. Furthermore, it was found that no additional color developed when air was passed through the mixture of oxygen-free sample and reagent, a fact which indicates complete destruction of peroxides largely by decomposition rather than reduction. It therefore appears that dissolved oxygen is necessary in this method, either to speed up the reduction reaction or to inhibit the ferrous ion–catalyzed decomposition.

As a result of these studies, the colorimetric method is recommended as the best for frequent analyses of materials containing only small amounts of peroxides. For materials (except diolefins) containing large amounts of peroxides, the iodometric method is more precise and accurate. The colorimetric method is not well suited for materials containing polymer, particularly diolefins, because of turbidity caused by insoluble high polymers.

ANALYTICAL METHOD

Apparatus. A Spekker photoelectric absorptiometer was used, equipped with blue No. 6 and green No. 5 filters and absorption cells allowing the light to pass through a layer of solution 1 cm. thick.

Reagent. Ferrous thiocyanate solution was prepared as follows: Dissolve 1 gram of C.P. ammonium thiocyanate and 1 ml. of 25% by weight of sulfuric acid in 200 ml. of C.P. deaerated methanol, and shake the resulting solution with 0.2 gram of finely pulverized ferrous ammonium sulfate. Place the decanted reagent (prepared fresh daily) in a brown glass-stoppered bottle.

Procedure. Introduce 1 ml. of sample preferably containing between 0.0001 and 0.0007 milliequivalent of reactive peroxide into a 25-ml. volumetric flask. (If necessary, use 1 ml. of a suitable methanol dilution of the sample.) Fill to the mark with ferrous thiocyanate reagent, mix well, and fill the colorimeter cell with the mixture. At 10 minutes from the time of mixing, read the optical density and convert the value, corrected by a blank determination, to terms of concentration by comparing it with the optical density calibration curve obtained by use of corresponding known amounts of standard ferric chloride solutions.

EXPERIMENTAL

Materials Used. Samples of tetralin peroxide, cumene peroxide, *tert*-butyl hydroperoxide, and 30% hydrogen peroxide and autoxidized samples of diisobutylene, 2-pentene, cyclohexene, methylpentadiene, and diethyl ether were identical with those used in experiments reported in a previous paper (*6*).

Applicability and Accuracy. The listed materials were analyzed by the colorimetric method and also by the sodium iodide–isopropyl alcohol method (*6*). Results, given in Table I, show that

Table I. Accuracy of Colorimetric Peroxide Method Compared to Sodium Iodide–Isopropyl Alcohol Method

Material	Sodium Iodide–Isopropyl Alcohol Method	Colorimetric Method
Apparent Peroxide Content, %		
tert-Butyl hydroperoxide	99.8	105
Cumene peroxide	94.2	112
Tetralin peroxide	95.4	95
Hydrogen peroxide, 30%	29.2	24
Peroxide No., Milliequivalents per Liter		
Cyclohexene	121	120
2-Pentene	51	48
Diisobutylene	19.7	19
Diethyl ether	12.2	7.4
Methylpentadiene	61	266

Table II. Effect of Sample Size and Reaction Time on Results for Autoxidized Methylpentadiene by Colorimetric Peroxide Method

Sample Dilution in Methanol	Peroxide No., Milliequivalents per Liter[a]				
	2.5 min.	5 min.	10 min.	20 min.	40 min.
1:500	170	230	300	365	430
1:1000	160	230	300	360	410

[a] Referred to original sample before dilution.

Table III. Effect of Sample Size on Results by Colorimetric Peroxide Method

Sample	Dilution	Peroxide No., Milliequivalents per Liter
tert-Butyl hydroperoxide in methanol	40.2 mg./l.	0.96[a]
	20.1 mg./l.	0.48[a]
Cyclohexene	1:200	98 to 104
	1:400	108 to 112
Diisobutylene	1:25	16 to 17
	1:50	16 to 17
2-Pentene	1:200	62 to 70
	7:4000	46 to 57
Diethyl ether	1:5	2.35
	1:10	2.20

[a] Results quoted on dilute solution of pure peroxide; all others refer to original sample before dilution.

the two methods agree reasonably well in most cases. Poor agreement was obtained on ether and methylpentadiene (a conjugated diolefin). In the latter case, the reduction reaction was slow and incomplete with both methods, indicating that both disagreeing results were of only empirical value. Benzoyl peroxide also reacted only slowly with the ferrous thiocyanate reagent. Since results close to theoretical (considering the low precision of the colorimetric method) were obtained on the pure hydroperoxides, there is reason to believe that the colorimetric method is fundamentally accurate when applied to autoxidized materials containing only isolated double bonds.

Effects of Sample Size and Reaction Time. The hydroperoxides react quickly; the optical density increases rapidly during the first 2 minutes and thereafter remains constant. However, the peroxides in methylpentadiene, which are presumably of the bridge type described by Bodendorff (*1*), react very slowly, as shown in Table II. Sample size does not seem to influence results appreciably on any of the materials tested, as shown in Tables II and III. The absence of an effect of sample size with methyl pentadiene seems odd in view of the pronounced effect of this variable on results for conjugated diolefins by the sodium iodide method.

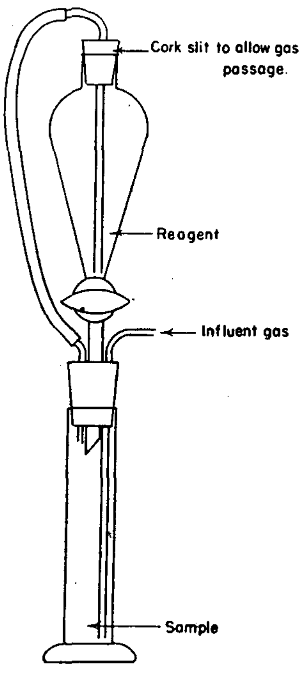

Figure 1. Apparatus for Changing Dissolved Gas in Reagent and Sample before Mixing

Effect of Oxygen Concentration. In order to remove dissolved oxygen from the sample and reagent before mixing, an apparatus similar to that described by Lea (*4*) was used (Figure 1). Nitrogen, from which oxygen had been removed by passage over copper at 700° C., was passed for 10 minutes through the 1 ml. of sample in the cylinder and then through the reagent in the funnel. At the end of this period the reagent was allowed to mix with the sample, and a portion of the mixture was removed (with nitrogen being bubbled through the solution) via a nitrogen-filled pipet to fill a colorimeter cell, through which nitrogen was passed by means of a special cover (Figure 2). After a glass stopper was placed in the ground joint and the stopcock closed, the tubing conveying the nitrogen was removed and the optical density of the solution determined.

The third column of Table IV substantiates the observation of Lea (*4*) that much lower results are obtained in the absence of oxygen. As a check on the effect of the passage of gas through the materials, air was passed through the sample and reagent before mixing in exactly the same way as for nitrogen. The second column shows that good agreement is obtained with the results by the prescribed method except in the case of pure tetralin peroxide, which is somewhat anomalous. When air was added after mixing the deaerated sample and reagent, no deepening of color occurred, as shown in the fourth column. This demonstrates that the peroxide (nondiolefin) is completely and rapidly destroyed in the presence of ferrous ion, by both reduction and decomposition. In the presence of molecular oxygen, the reduction reaction takes place much more rapidly than the decomposition reaction; in the absence of molecular oxygen the reverse is true and only a small quantity of ferric thiocyanate is formed. Use of oxygen in place of nitrogen gave approximately normal values, verifying the conclusion that a certain amount of oxygen is necessary to obtain quantitative results and that the effect is not one of oxidation of ferrous ion by molecular oxygen.

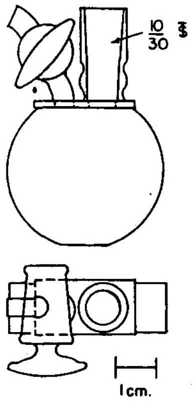

Figure 2. Colorimeter Cell with Cover for Air Exclusion

Table IV. Effect of Oxygen Concentration on Results by Colorimetric Peroxide Method

Sample	Prescribed Procedure	10 Min. Air, Then Mixed	10 Min. N_2, Then Mixed	10 Min. N_2, Mixed, Then 5 Min. Air	5 Min. O_2, Then Mixed
	Apparent Peroxide Content, %				
tert-Butyl hydroperoxide in methanol	94	96	63	56	...
Tetralin peroxide in methanol	98	68	4	6	91
29.4% hydrogen peroxide in methanol	23.5	...	15.4	15.4	...
	Peroxide No., Milliequivalents per Liter				
Cyclohexene	120	120	20	44	108
2-Pentene	48	53	11	11	...
Diisobutylene	19	21	4	4	...
Methylpentadiene	266	246	193	180	...
Diethyl ether	2.3	...	0.8	0.8	...

In the absence of oxygen lower values are also obtained on methylpentadiene, although the degree of lowering is less marked. The presence or absence of oxygen seems to have no influence on the rate of reduction of those peroxides remaining after mixing, since the optical density after mixing increases slowly and at about the same rate whether oxygen is present or not. This suggests that the hydroperoxides are destroyed rapidly upon mixing the reagent and sample, leaving only the bridge-type peroxides intact.

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Evaluation of the Ferrous-Titanous Method

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The ferrous-titanous (Yule and Wilson) method has been tested on a variety of autoxidized hydrocarbons and peroxides, including some pure peroxides of a type known to be present in autoxidized materials. The method generally gives results that represent only fractions of the true values. Precise results were obtained with peroxides in mono-olefins under ordinary conditions of application of the method, but it was necessary to control the experimental conditions carefully for precise results with diolefin peroxides. Being precise, the method has empirical usefulness if the results can be correlated with properties of the material in question. The method is convenient for multiple analysis, with the single disadvantage that initial preparation and storage of the reagents are more difficult than with other methods.

IN 1931, Yule and Wilson (*9*) reported that peroxides in gasolines could be quickly and conveniently determined by reducing them with ferrous thiocyanate in aqueous acetone and titrating the resulting ferric thiocyanate with standard titanous solution. They used results obtained in this way chiefly as a measure of the gum-forming tendencies of the gasoline, and stated that other methods were less suitable, although they recognized that the results by the ferrous-titanous method did not represent actual peroxide content. The latter fact was evident in view of dependence of results on sample size and of the observation that certain materials treated with ferrous sulfate contained peroxides capable of oxidizing iodide ion. Their choice of the ferrous-titanous method over the iodometric methods was based on the greater sensitivity of the ferrous-titanous method compared with that of the Marks and Morrell method (*5*), with which high and variable blanks are obtained [the blanks by the modified Kokatnur and Jelling method (*3, 7*) are negligible].

Evidence has been obtained (*6, 7*) that the sodium iodide–isopropyl alcohol method adapted from that of Kokatnur and Jelling (*3*) and the ferrous thiocyanate colorimetric method of Young, Vogt, and Nieuwland (*8*) are both basically accurate for the determination of peroxides in autoxidized materials which contain no conjugated diolefins. It was found that both methods give only empirical results on conjugated diolefin samples because of the slow rate at which such peroxides are reduced and possibly because of side reaction. In continuation of this study and in view of the wide use of the Yule and Wilson method, particularly in the petroleum industry, studies were made to determine its fundamental accuracy in the determination of peroxides in autoxidized materials and to compare it with other methods. Since the correction factors and dilutions prescribed by Yule and Wilson (*9*) were admittedly arbitrary, they have not been applied in the work described in this paper.

Specific peroxides of known purity, such as tetrahydronaphthyl hydroperoxide (tetralin peroxide), α,α-dimethylbenzyl hydroperoxide (cumene peroxide), *tert*-butyl hydroperoxide, benzoyl peroxide, and hydrogen peroxide gave results ranging from 12 to 80% of theoretical, with rather precise values for any given material. Results on autoxidized materials (nondienes) were generally from 20 to 60% of those by the sodium iodide method. Therefore, the evidence was strong that results by the ferrous-titanous method are generally very low. Yule and Wilson ascribed this tendency to decomposition of peroxides in the presence of ferrous ion to form nonoxidizing products (such reactions with tetralin peroxide and other peroxides are well known), and stability of some peroxides toward reduction by ferrous ion.

Yule and Wilson did not report the effect of molecular oxygen concentration on results by their method, but Lea (*4*), employing a similar method, proved that values with air excluded were only a fraction of those obtained by the usual procedure performed in the presence of air. He concluded that atmospheric and dissolved oxygen was oxidizing ferrous ion in the presence of peroxide and that in the absence of peroxides such an oxidation was insignificant. The effect of lack of oxygen had previously been recognized by the present authors, who had drawn similar conclusions. However, in no cases were the values obtained known to be higher than the theoretical ones.

In the light of later studies with the colorimetric method (*2*) which indicated that values obtained on autoxidized rubber samples were in no case higher than warranted by the amount of oxygen absorbed by the rubber, it seemed more likely that oxygen either catalyzes the reduction reaction or inhibits the ferrous ion–catalyzed decomposition reaction. Failure to obtain quantitative reduction of peroxides of known purity by the Yule-Wilson method even in the presence of oxygen is ascribed to too low a ratio of dissolved oxygen to peroxide, this ratio being of the order of only one hundredth of that obtaining with the ferrous thiocyanate colorimetric method. The dependence of results upon sample size (peroxide concentration) is thought to be closely related to the oxygen effect.

With the assumption that the relative results obtained by this method can be correlated with other properties of the material, and hence can be useful, the extent of dependence of precision on the manipulative variables was studied. On conjugated diolefins, results were found to be critically dependent on sample size, time of reaction, and temperature; on the rapidly reacting nondienes, only sample size had any effect.

ANALYTICAL METHOD

Reagents. Ferric chloride solution, standard 0.1 *N*.

Ferrous thiocyanate solution, prepared by dissolving 5 grams of ferrous sulfate and 5 grams of ammonium thiocyanate in 500 ml. of distilled water and 500 ml. of acetone. Add about 1 gram of pure iron wire and 5 ml. of concentrated sulfuric acid and expel air by passing hydrogen or carbon dioxide through the solution. Store the solution in an all-glass system under hydrogen; use when the red color has disappeared.

Titanous sulfate solution, standard 0.01 *N*, prepared as follows: Heat a mixture of 20 ml. of C.P. concentrated sulfuric acid and 80 ml. of water to 70° C. and add in small portions 0.6 gram of titanium hydride powder (obtainable from Metal Hydrides, Inc., Beverly, Mass., under the trade name Altertan). When the reaction subsides, boil the solution on a hot plate for 2 minutes, then pour it into about 900 ml. of distilled water freshly deaerated with carbon dioxide. After the undissolved material has settled, siphon the supernatant liquid into a dark storage bottle previously filled with carbon dioxide. Store the solution under hydrogen, dispense from an all-glass system, and standardize daily against the standard ferric chloride solution in the presence of thiocyanate ions.

Procedure. Measure 50 ml. of ferrous thiocyanate solution into a 250-ml. glass-stoppered Erlenmeyer flask and discharge any red color with the minimum amount of titanous solution. Bring the solution to 25° ± 2° C., add the sample containing up to 5 milliequivalents of peroxide, stopper the flask, shake vigorously for 5 minutes ±5 seconds, and titrate with standard titanous solution to the disappearance of the red color.

Table I. Comparison of Results on Known Peroxides by Ferrous-Titanous and Sodium Iodide–Isopropyl Alcohol Methods

Peroxide	Peroxide Concentration	Peroxide Purity Found			
		Sodium iodide method		Ferrous-titanous method	
	G./l.[a]	*Per cent by weight*			
Tetralin peroxide	7.92	98.3	98.4	25.5	27.0
Cumene peroxide	13.86	94.2		73.5	
tert-Butyl hydroperoxide	6.59	98.3	98.5	78.7	79.1
Hydrogen peroxide (29.9%)	11.59	29.4		12.2	
Benzoyl peroxide	10.10	98.7	99.0	13.6	13.9
Ascaridole	8.40	25.7		31.7	

[a] Benzene (C.P. thiophene-free) used as solvent except in case of hydrogen peroxide, which was dissolved in water. 5 ml. of solution used in all cases.

EXPERIMENTAL

Materials Used. Samples of tetralin peroxide, cumene peroxide, *tert*-butyl hydroperoxide, 30% hydrogen peroxide, benzoyl peroxide, and ascaridole, and autoxidized samples of diisobutylene, 2-pentene, cyclohexene, tetralin, methylpentadiene, isoprene, and diethyl ether; these were identical with those used in experiments reported in previous paper (*7*).

Accuracy. The method was applied to several of the known peroxides in order to check its accuracy. As shown in Table I, the recoveries with hydroperoxides are invariably far below theoretical or below that for the sodium iodide–isopropyl alcohol method.

Of the peroxides tested, only tetralin peroxide and cumene peroxide were formed by natural autoxidation, but the results obtained on those demonstrated that the ferrous-titanous method is inaccurate on even the simplest peroxides, whereas the iodometric method gives satisfactory accuracy (*7*). The fact that the ferrous-titanous results are dependent on sample size indicates, however, that it may be possible to obtain theoretical results on samples containing only very small amounts of peroxides. Comparative data obtained on typical samples of autoxidized materials are shown in Table II.

Table II. Comparison of Results on Autoxidized Materials by Ferrous-Titanous and Sodium Iodide–Isopropyl Alcohol Methods

Material[a]	Peroxide No., Milliequivalents per Liter	
	Sodium iodide method	Ferrous-titanous method
Diisobutylene	35.7, 36.9	25.2
2-Pentene	40.8, 41.6	16.0, 15.9
Cyclohexene	85.0, 84.5	20.6, 20.6
Tetralin	91.4, 90.8	18.6, 18.0
Diethyl ether	12.2, 12.4	7.2, 7.4
Methylpentadiene	65.9, 68.5	88.0, 82.2
Isoprene	58.8, 57.1	67.7, 66.1

[a] 5 ml. of sample used in all cases.

Comparison of the analyses of the nondiolefinic samples shows considerable similarity with results on pure hydroperoxides. This result is expected, since it has been shown that the initial products of autoxidation of olefins are, in fact, hydroperoxides. On the other hand, Bodendorff (*1*) has shown that conjugated diolefins form bridge-type peroxides by 1,4- addition of molecular oxygen intramolecularly or intermolecularly. These substances react slowly with ferrous ion as well as with iodide ion, the results with both methods being purely empirical. Ascaridole, a pure monomeric 1,4 bridge-type peroxide, behaves in the same manner, reacting slowly and incompletely with both iodide ion and ferrous ion.

Oxygen Effect. In order to test the oxygen effect, noted by Lea (*4*), experiments were performed in which carbon dioxide or oxygen was passed through the reagent for 2 minutes before adding the sample and shaking the mixture, and also during the titration. Results, compared with those obtained with an air atmosphere, are shown in Table III. Blank corrections, which were always very small, were applied in each case.

The dependence on oxygen concentration is very evident. Moreover, as was the case with the colorimetric method (*6*), no further coloration appears upon passage of air or oxygen into the mixture after a sample of an autoxidized nondiolefin has been reduced under carbon dioxide and titrated. This indicates that the peroxides have been entirely destroyed, though they have been only partially reduced by ferrous ion. This is evidence for the conclusion that oxygen either catalyzes the reduction reaction or inhibits the decomposition reaction.

In contrast to the colorimetric method, results even in the presence of pure oxygen are considerably below theoretical. These results are understandable if one assumes that the concentration of oxygen necessary for quantitative reduction of the peroxides is dependent upon the peroxide concentration; the ratio of dissolved oxygen to peroxide is roughly one hundredth as great with the ferrous-titanous method as with the colorimetric method (*6*).

Table III. Effect of Oxygen Concentration on Results by Ferrous-Titanous Method

	Purging Gas Used		
	CO_2	Air	O_2
	Apparent Peroxide Content, %[a]		
Tetralin peroxide	6.4	24.0	56.9
Cumene peroxide	58.3	73.2	..
tert-Butyl hydroperoxide	57.1	61.8	64.2
Hydrogen peroxide	11.7	12.2	13.8
Benzoyl peroxide	15.4	18.8	18.0
Ascaridole	9.2	31.7	39.2
	Peroxide No., Milliequivalents per Liter		
Diisobutylene	1.3	2.2	2.4
2-Pentene	5.2	17.6	30.7
Cyclohexene	6.7	20.6	46.8
Tetralin	2.2	16.9	41.1
Methylpentadiene	2.4	23.8	23.8
Isoprene	9.0	60.0	65.3
Diethyl ether	3.6	7.4	..

[a] Hydrogen peroxide diluted with water; all other known peroxides dissolved in C.P. benzene. 5-ml. samples used.

Table IV. Effect of Time of Shaking and Sample Size in Determination of Known Peroxides by Ferrous-Titanous Method

	Apparent Peroxide Content, %W of Original Sample					
	Time of Shaking			Sample Size		
	1 min.	5 min.	15 min.	10 ml.	5 ml.	2 ml.
Tetralin peroxide	23.1	22.1	24.5	20.6	22.1	39.1
tert-Butyl hydroperoxide	80.8	80.6	80.6	68.8	80.6	90.0
Hydrogen peroxide[a]	14.8	14.1	14.0	13.5	14.1	14.5
Benzoyl peroxide	6.5	15.0	31.9	..	15.0	27.1
Ascaridole	31.7	31.7	30.4	29.2	31.7	38.7

[a] Solutions in water; all others made up in C.P. benzene, about 10 grams per liter. Hydrogen peroxide original solution actually about 30%. 5 ml. samples used unless otherwise specified.

Table V. Effect of Manipulative Variables on Results for Autoxidized Materials by Ferrous-Titanous Method

	Peroxide No., Milliequivalents per Liter							
	Time of Shaking			Sample Size			Reaction Temperature[a], ° C.	
Material	1 min.	5 min.	15 min.	10 ml.	5 ml.	2 ml.	15	30
Diisobutylene	2.0	2.2	2.2	2.0	2.2	...	2.2	2.2
2-Pentene	17.7	17.6	16.5	..	15.7	21.5	17.4	15.6
Cyclohexene	29.0	29.4	27.0	..	29.4	45.8	23.5	21.6
Tetralin	21.8	20.8	22.0	..	20.9	40.0	18.2	16.8
Diethyl ether	8.3	8.2	7.3	7.5	8.2	8.6	..	..
Isoprene	25	60	103	36	64	99	37.8	70.1
Methylpentadiene	43	90	140	..	90	144	13.7	29.3

[a] Obtained in special water-jacketed flask, with reagent and flask brought to temperature before addition of sample.

Dependence on Manipulative Variables. In the light of the data, the ferrous-titanous method appears to be empirical, and useful only if values obtained by it are reproducible and correlate well with some property of the test material significant to application, such as explosion hazard or gum-forming tendency. Such correlations can only be tested by experiments on the particular material in question. In order to test the dependence of precision on the experimental conditions of the method, various materials were analyzed using variations in time of shaking, sample size, and reaction temperature. Results (Tables IV and V) show that the behavior of peroxides in conjugated diolefins is in sharp contrast with those obtained from compounds with isolated double bonds or ether linkages. Peroxides in conjugated dienes are slow reacting and results are affected by sample size, temperature, and oxygen concentration. Peroxides in the other materials react almost instantaneously, and results depend only on oxygen concentration and, to a lesser extent, on sample size. These results are consistent with the fact that peroxides in mono-olefins, and probably those in ethers, are the rapidly reacting alkyl hydro peroxides, whereas those in conjugated diolefins are the slow-reacting bridge-type peroxides. It is evident that with the latter, precise results are obtainable only if variables in the analysis are controlled rather closely. Benzoyl peroxide is a special case, reacting fairly rapidly with iodide ion but only slowly with ferrous ion. Ascaridole, though it is a typical diolefin peroxide monomer, seems to react rapidly in contrast to autoxidized diolefins. The slow-reacting diolefin peroxides may be the polymeric peroxide types mentioned by Bodendorff (1) rather than the monomeric bridge-type forms.

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Gravitometry of Heavy Water

New Reference Liquids for the Falling-Drop Method and Precision Attainable

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Solutions of phenanthrene in α-methylnaphthalene are used as reference liquids in measuring the specific gravity of water samples having D_2O contents ranging from 10 to 40%. Properties of these solutions and the precision of the falling-drop method are discussed.

THE falling-drop method has been used extensively to determine the specific gravity of small quantities of heavy water. Barbour and Hamilton (*1, 2*) first applied the essential principles of the method to a study of biological fluids, but soon thereafter Vogt and Hamilton (*7*) and Fenger-Eriksen (*3*) adapted the techniques for heavy water analysis. In this method, a drop of water of fixed volume is allowed to fall through a bromobenzene and xylene mixture which has a slightly lower specific gravity than the water sample. The time required to fall a fixed distance is measured and from this the specific gravity of the water or its deuterium oxide concentration is found by referring to a calibration curve. In order to eliminate a troublesome correction for temperature variations, it is customary to keep the tube which contains the reference liquid in a thermostated bath held within a few thousandths of a degree of a predetermined setting. Finally, several mechanical pipets have been proposed to obtain reproducibly water drops of constant volume (*4, 6*).

There is a distinct disadvantage in the use of bromobenzene and xylene mixtures as reference liquids. Since these liquids are volatile and have different boiling points, a slight amount of evaporation causes a change in density of the mixture which remains and makes it necessary to recalibrate the system frequently. Keston, Rittenberg, and Schoenheimer (*5*) overcame this disadvantage for water having low deuterium oxide content by substituting *o*-fluorotoluene, a single liquid, for the two-component mixture. While this compound is very satisfactory for low-density samples, it is not suitable for water which has a deuterium oxide content much above 7%, for the precision of the falling-drop method falls off rapidly as the difference in density of the water and reference liquid increases. Water samples of high specific gravity may of course be diluted until they are within the indicated range, but this is a tedious procedure and errors are likely to occur.

In the course of investigating the exchange reaction between cellulose and heavy water, it became necessary to measure the specific gravity of water samples which had deuterium oxide contents ranging from 20 to 25%. For this purpose it was found that solutions of phenanthrene in α-methylnaphthalene could be used as reference liquids. These solutions are superior to bromobenzene-xylene mixtures, since neither component is particularly volatile, and in addition the composition can be varied so as to accommodate water samples which contain from 11 to about 40% deuterium oxide. In this paper the properties of these solutions are described, with a study of the precision of the falling-drop method.

APPARATUS

The apparatus constructed for this work was essentially a duplicate of the one described by Rittenberg (*5*). Perhaps the only significant change was that the falling time of the water drop was measured for a 10-cm. distance instead of 15 cm. The viscosity of α-methylnaphthalene is considerably higher than for the reference liquids in prior use and the shorter distance was used therefore to compensate for the slower rate of fall. The falling time was measured with a synchronous motor electric stopwatch which could be read to the nearest 0.1 second.

The apparatus proper consists of two units: a high-precision thermostat and a mechanical micropipet. In the authors' work the thermostat was set at 26° C., was very efficiently agitated, and maintained the temperature so constant, that no movement could be observed on a Beckman thermometer. The micropipet was constructed after the design suggested by Rosebury (*6*), and was calculated to have a delivery of 9 cu. mm.

REFERENCE LIQUIDS

The two ingredients used in the reference liquids can be obtained commercially. Very little laboratory purification is required, since there are products available which are reported to be free of phenols and other ingredients that might diffuse into the water drops and cause some difficulty.

The α-methylnaphthalene (primary Diesel fuel grade) was obtained from the Reilly Tar and Chemical Corporation and prior to use was vacuum-distilled at 70° to 80° C. and 1 mm. The middle fraction, consisting of about one third of the total charge, was retained. This portion was a light straw-colored liquid of thin, oily consistency which did not discolor or darken even after it was stored for one year. Commercial refined phenanthrene, an off-white crystalline product, was used as supplied by the same concern.

The specific gravity of the reference solutions depends on the concentration of phenanthrene and the temperature setting of the thermostat. In order to find the relationships of these variables, the specific gravity was determined over a range of temperatures for the retained fraction of α-methylnaphthalene as well as for two solutions, one made by adding 15 grams of phenanthrene to 100 grams of α-methylnaphthalene, the other by adding 30 grams. It was found convenient to use a 25-ml. specific gravity bottle fitted with a ground-glass thermometer for the measurements. The weight of distilled water contained by the bottle was measured at three temperatures in the range of 20° to 30° C., thus permitting interpolation for intermediate temperatures. The indicated temperatures were chosen because they are the practical limits within which one is likely to operate the bath for the falling-drop apparatus.

The results of the specific gravity measurements are shown in Figure 1. It can be seen that the lightest reference liquid is given by α-methylnaphthalene at 30° C. Since the specific gravity at this point is 1.010, the lowest concentration of heavy water that can be determined is 10% deuterium oxide. By the same token, if one uses a nearly saturated solution that has a specific gravity of 1.040, the specific gravity of water that contains from about 37 to 42% deuterium oxide can be measured accurately. Thus, by choosing the appropriate concentration of phenanthrene, heavy water of from 10 to 42% deuterium oxide content may be analyzed. Because the lines for the three reference liquids in Figure 1 are essentially parallel, it is possible to represent the specific gravity of the phenanthrene-α-methylnaphthalene system as a family of lines with concentration and temperature as parameters. Thus in the temperature range of 20° to 30° C.,

$$S_0 = 1.011 + 0.001\,C + 0.0004\,(30 - t^\circ)$$

where S_0 = specific gravity reference solution at t°/t°

C = grams of phenanthrene added per 100 grams of α-methylnaphthalene

and t° = temperature of thermostat in ° C.

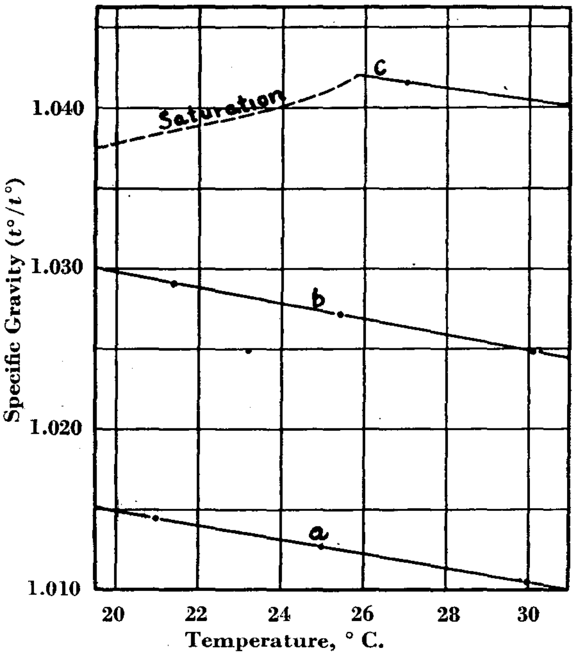

Figure 1. Temperature–Specific Gravity Relationships

a. Pure α-methylnaphthalene
b. α-Methylnaphthalene plus 15% added phenanthrene
c. α-Methylnaphthalene plus 30% added phenanthrene

The expansion and contraction of the reference liquid with small temperature fluctuations of the thermostated bath will have some influence on the precision of the analyses. To estimate the magnitude of this influence, the slope of the lines in Figure 1 may be examined. If one ignores the change in the radius of the water drop with temperature, a change of 0.01° C. in the bath results in an error of only 5 parts in the sixth decimal place of the specific gravity. Thus, the expansivity of the proposed reference liquids is sufficiently small, especially if one remembers that the thermostat maintains the temperature constant to a few thousandths of a degree, so that at most the error from residual temperature fluctuations should be not more than one or two parts in the sixth decimal of the specific gravity.

LINEARITY OF CALIBRATION CURVE

It is customary to calibrate the falling-drop apparatus by using samples of known specific gravity.

Table I. Calibration of Falling-Drop Apparatus

Point No.	Falling Time, t (Sec.)	Specific Gravity by Pycnometer	Specific Gravity from Equation 2	Difference
1	134.7	1.02293	1.022925	0.000005
2	94.2	1.02343	1.023433	0.000003
3	66.4	1.02413	1.024142	0.000012
4	55.8	1.02461	1.024601	0.000009
5	36.0	1.02619	1.026166	0.000024
6	23.7	1.02871	1.028462	0.000248

The falling time is related to the specific gravity by a linear expression derivable from Stokes' law (*5*):

$$S = S_0 + \frac{b}{t} \qquad (1)$$

where S = specific gravity of heavy water
S_0 = specific gravity of reference liquid
b = a constant
t = time required for drop to fall a fixed distance

For precise analyses, measurements are usually restricted to drops that fall slowly—i.e., drops for which the specific gravity is close to S_0. Two reasons exist for this limitation; Equation 1 does not hold for drops which fall rapidly, because they deviate considerably from a spherical shape; and, as is shown below, the precision deteriorates rapidly as t becomes small.

In the work for which this method was to be used, it was important to investigate the range of deuterium oxide concentrations for which Equation 1 was valid, in order to decide whether to prepare one or more reference liquids. A solution of phenanthrene in α-methylnaphthalene was made up which had a specific gravity of about 1.022, since samples of from 23 to 25% deuterium oxide content had to be analyzed. For calibration, a series of heavy water samples, freed from dissolved air by distillation immediately prior to use, was studied. The specific gravities of the samples were determined by use of a pycnometer, sufficient care being taken to ensure an accuracy of one part in the fifth decimal place. The falling times of these samples were determined in quadruplicate and the data which resulted are shown in the first columns of Table I.

A preliminary examination of the data indicated that the first four samples which were studied would probably fit a straight line with good accuracy. Accordingly, the necessary computations were carried out to find the least squares values of S_0 and b for Equation 1, using only the data for the first four points. The final equation was found to be

$$S = 1.021741 + \frac{0.15942}{t} \qquad (2)$$

To evaluate the closeness of fit for the calibration points as well as for the last two samples, the observed values for t were inserted in Equation 2. The specific gravities found by computation are compared with the values obtained by pycnometry in the last two columns of Table I.

The deviations indicate that the first four points are linearly related with an accuracy of about one part in the sixth significant figure of the specific gravity, which is also the accuracy of the pycnometer values. The first and fourth points correspond to 21.2 and 22.8% deuterium oxide, respectively, and since linearity probably holds for concentrations somewhat beyond these limits, the data show that the proposed reference liquids can be used for a 2% range of heavy water concentration. The analyses within that range should be accurate to 0.01% deuterium oxide. If one does not need such accuracy, a least squares fit extending over the region of the first five points might be used, in which case a 3 to 3.5% range of concentrations could be utilized with an accuracy of 0.02% deuterium oxide. Beyond this range the curvature of the calibration begins to increase very rapidly and the use of more than one reference liquid or some other expedient (*4*) is indicated.

The linear range observed in this study is larger than that reported for reference liquids in prior use; it is twice as large—e.g., as for *o*-fluorotoluene (*5*)—if the comparison is based on the same goodness of fit. The explanation for the difference is perhaps related to the higher viscosity of α-methylnaphthalene as compared to *o*-fluorotoluene; while the exact viscosity coefficient for the latter is not available, by inference from similar compounds one may estimate the value for the former to be about three times as large as that for *o*-fluorotoluene. As a result, for the same specific gravity difference between the reference liquid and the heavy water, a drop in α-methylnaphthalene will fall more slowly and remain more nearly spherical over a wider range of deuterium oxide concentrations. Finally, bromobenzene-xylene mixtures would also have comparatively low viscosity coefficients, so that for these liquids too a linear region of about 1% would be expected.

PRECISION

The precision that is attainable with a falling-drop apparatus depends on a number of factors. The first of these is the magnitude of the change in density of the drop as it falls through a column saturated with water of a different density. While it is difficult to estimate this magnitude, the data in Table II indicate that it is very small. Failure of the water to be at the temperature of the suspension medium is another factor that must be considered; such a condition results in an error in the size of the drop. It can be shown by direct calculation that this error is eliminated by maintaining the falling-drop apparatus in a constant-temperature room as was done in the work described in this paper.

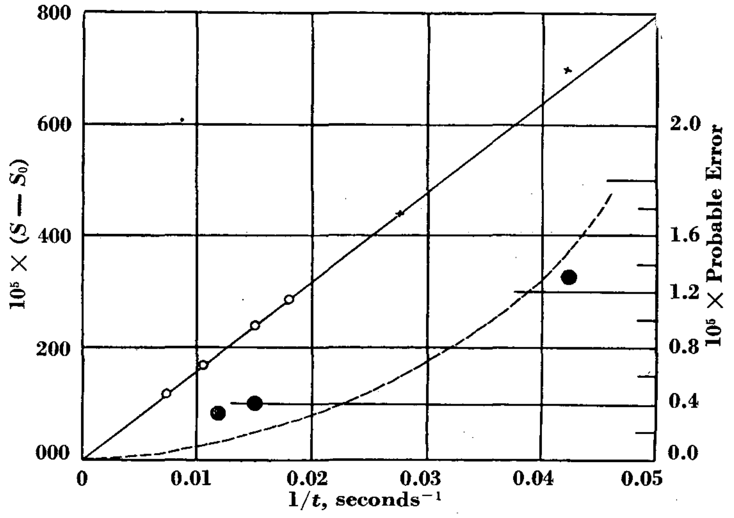

Figure 2. Calibration and Error Curves

—. From least squares equation
○. Calibration points, high-precision range
×. Other points, low-precision range
----. Calculated p_T curve from Equation 4
●. Observed probable error, p_S (cf. Table II)

Three important sources of experimental error which bear an interesting relationship to one another are (1) temperature fluctuations of the thermostat, (2) variations in the size (radius) of the drop, and (3) errors in timing the fall of the drop.

Table II. Observed Precision

Observed Falling Time, Seconds	
84.5, 85.0, 85.2, 84.9, 85.2, 84.9, 85.1, 84.7, 84.8, 84.7, 84.9, 85.0, 84.9, 84.5, 85.2, 84.6, 84.7, 84.8, 85.1, 85.0	Mean specific gravity = 1.023619, $p_s = 3.2 \times 10^{-6}$
66.4, 66.5, 66.6, 66.1, 66.5, 66.2, 66.2, 66.6, 66.1, 66.3, 66.3, 66.4, 66.6, 66.6, 66.4, 66.5, 66.5, 66.2, 66.5, 66.5	Mean specific gravity = 1.024142, $p_s = 4.0 \times 10^{-6}$
22.5, 22.5, 22.6, 22.4, 22.6, 22.5, 22.5, 22.5, 22.5, 22.6, 22.5, 22.7, 22.6, 22.5, 22.5, 22.5, 22.5, 22.5, 22.5, 22.6	Mean specific gravity = 1.028817, $p_s = 13 \times 10^{-6}$

If the probable error of the specific gravity due to each of these causes alone is p_t, p_r, and p_T, respectively, then p_s, the resulting error in the specific gravity when all sources are operative, may be written

$$p_s = \sqrt{p_t^2 + p_r^2 + p_T^2} \tag{3}$$

The influence of temperature fluctuations has already been indicated; p_t is a constant over the entire calibration range. If one were to graph the magnitude of the errors on the abscissa and $S - S_0$ on the ordinate, p_t would be represented by a horizontal straight line. By considering Stokes' law and its partial derivatives, it can be deduced that p_T is a straight line inclined to the abscissa and passing through the origin. By similar reasoning it can be shown that p_T is one arm of a parabola and like p_r it passes through the origin. The composite curve, p_s, is consequently a distorted parabolalike function which does not vanish as $S - S_0$ approaches zero, but instead it approaches the limiting value, p_t. That this should be so becomes obvious when one considers a drop of the same specific gravity as the reference liquid; such a drop will rise and fall about a mean position as the temperature fluctuates, but neither the radius of the drop nor timing will have any bearing on its behavior.

For a practical evaluation of the precision attainable with the apparatus used in the present study, twenty analyses were made on each of three heavy water samples. Two of the samples were in the high-precision region of the calibration curve and one was in the low-precision range. The data are reported in Table II.

The composite graph shown in Figure 2 demonstrates the relationship among the calibration curve, the experimental p_s values, and the calculated p_T curve. The latter is most easily constructed by multiplying the product of the ordinate and abscissa for various points along the calibration curve by the probable error of the falling time. This error was assumed to be 0.05 second in the authors' particular case, since the stopwatch could be read to 0.1 second, and the equation is consequently

$$p_T = (S - S_0) \times 1/t \times 0.05 \tag{4}$$

The observed errors are about twice as large as those calculated for timing alone; the difference in the main is probably due to temperature fluctuations with a small contribution from drop-size variations. In the low-precision region the observed error seems smaller than it should be, but this is probably due to assuming too large a value for the probable error of timing.

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Practical Test for Estimating Storage Stability of Gasolines

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A practical adaptation of the extrapolated gum time test for predicting the storage stability of gasoline is described. The original method required determination of gum times under several accelerated conditions to permit evaluation of test accelerants, temperature, and oxygen pressure. The modified procedure described comprises a single aging or gum time test under accelerating conditions, moderated to the extent that average effects may be assumed for test accelerants without introducing undue certainty in stability predictions. The test may be used for evaluation of the stability of both motor and aviation fuels, although examples are presented only for motor fuels at this time.

A RECENT publication by some of the present authors (*3*) describes an extrapolated gum time method for predicting the storage (gum) stability of gasoline from accelerated test measurements. This procedure involved determination of the rate of formation of gum under several accelerating conditions, followed by extrapolation of the results to given conditions of storage, thereby furnishing a prediction of the actual storage life. Predictions by this method were shown to correlate with actual storage measurement within the accuracy limits of experimental and extrapolated results, thus proving the validity of temperature and oxygen pressure effects involved in extrapolation. In the form presented, the extrapolated gum time method was unsuited for general application, being too lengthy and requiring exacting precision, since small errors in accelerated test measurements became greatly magnified on exponential extrapolation.

A modification of the extrapolated gum time procedure has been developed and is presented herewith. In this modified gum time test, the accelerating effect of oxygen pressure is eliminated, and the effect of temperature is moderated to the extent that a single gum time or aging gum determination will give a reliable prediction of storage stability which is as accurate as the longer method and yet insensitive to the effect of experimental error. In essence, the modified gum time test may be considered a storage test conducted at moderately high temperatures. In principle, therefore, it goes one step further than the Voorhees and Eisinger method (*2*) in the reduction and rationalization of accelerants commonly employed in gasoline stability measurements (*1*).

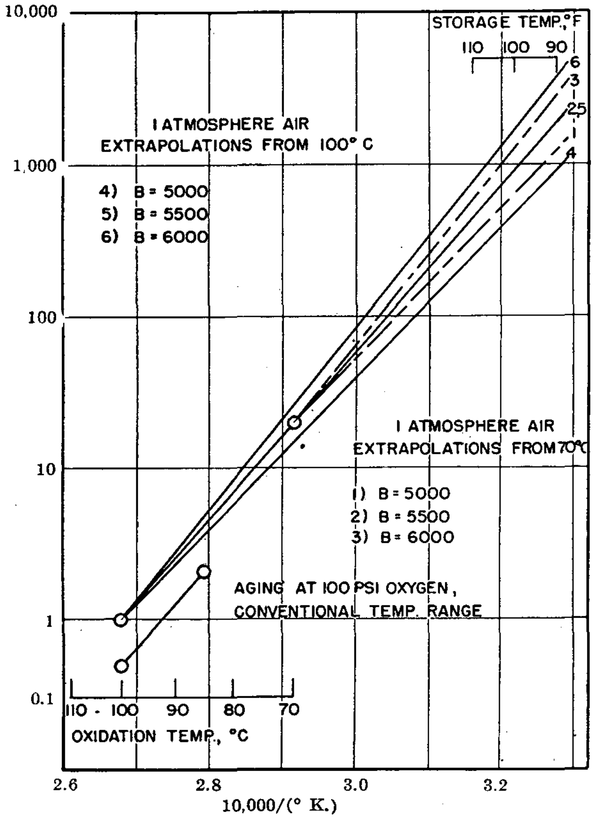

Figure 1. Magnitude of Extrapolations for Modified and Detailed Gum-Time Methods

Throughout this paper, all gum measurements are in accordance with A.S.T.M. Method D38–142, while gum times refer to the time required to reach given A.S.T.M. gum contents (5-mg., 10-mg., etc.) under the specified conditions of aging. Gum times as such may be determined from linear or semilogarithmic plots of A.S.T.M. gum *vs.* time of aging.

BASIS OF TEST

The following considerations show the basis for simplification of the extrapolated gum time test. The effect of temperature and oxygen pressure on gasoline stability can be expressed by the following equations:

Temperature Effect.

$$\log t_1/t_2 = B\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ (at a constant oxygen pressure)} \quad (1)$$

where t_1 and t_2 = gum times at respective temperatures
T = absolute temperature, ° K.
B = temperature coefficient

Oxygen Pressure Effect.

$$\log t_1/t_2 = D \log P_1/P_2 \text{ (at a constant temperature)} \quad (2)$$

where t_1 and t_2 = gum times at respective oxygen pressures
P = oxygen pressure, pounds per square inch absolute
D = oxygen pressure coefficient

Table I. *B* and *D* Values and Equivalent Time Ratios for Gasolines

Sample No.	Effect of Temperature *B* value	Effect of Temperature Time ratio[a]	Effect of Oxygen Pressure *D* value	Effect of Oxygen Pressure Time ratio[b]	Combined Effect of Temperature and Oxygen Pressure Time Ratio[c]
1	6180	6.4	−0.116	1.5	9.6
2	5250	1.8	−0.045	1.2	2.2
3	5160	1.6	−0.515	6.6	10.6
4	6010	5.1	−0.312	3.1	15.8
5	6050	5.4	−0.116	1.5	8.1
6	5280	1.9	−0.086	1.4	2.7
7	5110	1.5	−0.369	3.8	5.7
8	5070	1.4	−0.140	1.7	2.4
15	5880	4.3	−0.134	1.6	6.9
17	5150	1.6	−0.060	1.2	1.9
18	5320	2.1	−0.061	1.2	2.5
19	5830	4.1	−0.069	1.3	5.3
20	6030	5.4	−0.500	6.2	33.5
21	5060	1.4	−0.064	1.2(5)	1.8
22	5190	1.7	−0.048	1.2	2.1

[a] No. of months at 90° F. equal to 1 hour at 100° C.

[b] No. of hours at 1 atm. air equal to 1 hour at 100 p.s.i. oxygen.

[c] No. of months at 90° F. and 1 atm. air equal to 1 hour at 100° C. and 100 p.s.i. oxygen.

These equations differ from the usual forms (*3*) in that the intercept constants *A* and *C*, which have no general significance, have been eliminated.

Table I, extracted from (*3*), shows that the range of *B* values for a number of different gasolines lies in the range of about 5000 to 6000, averaging about 5500; these limits are confirmed by numerous other observations. Temperature extrapolations are normally made from 100° C. (test temperature) to, say, 90° F. (32.22° C., storage temperature). Assuming a *B* value of 5500, extrapolations for this temperature range could be in error by a factor of about 2 if *B* were actually 500 units smaller or larger than the assumed value. This possible uncertainty is greater than desired, but, as shown in Figure 1, could be cut down appreciably by reduction of test temperature, although at the expense of increased test time.

In addition to the uncertainty due to temperature, there is superimposed the effect of oxygen pressure, which, while small for some gasolines, is rather large for others. Oxygen pressure can be eliminated as a test accelerant, especially at lower temperatures (*4*), by conducting the aging test under 1 atmosphere air, provided a sufficiently high air-to-gasoline volume ratio is maintained so that oxygen depletion effects do not govern stability rates (*3*).

Accordingly, the simplified procedure comprises oxidation of gasoline under 1 atmosphere air at some temperature below

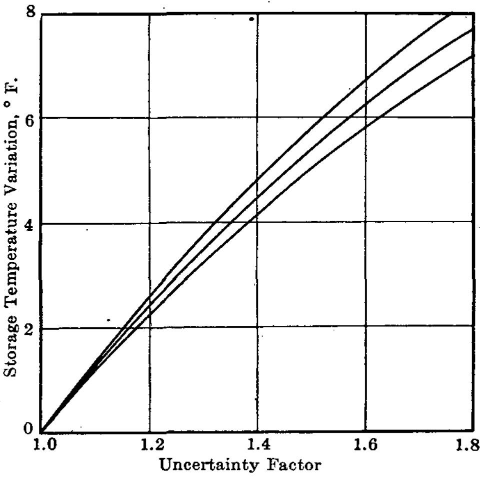

Figure 2. Relation between Uncertainty Factor and Variation in Storage Temperature for Constant Predicted Storage Life

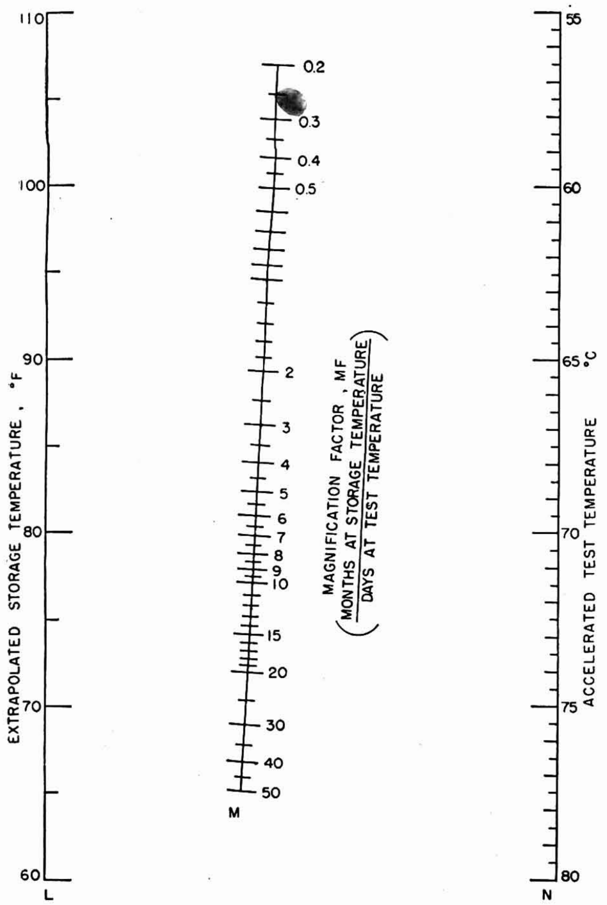

Figure 3. Magnification Factor Resulting When Extrapolating from Accelerated to Storage Temperatures

100° C., the results then being extrapolated to the desired storage temperature by assuming a B value of 5500. The uncertainty in the extrapolation from the simplified test arises primarily from the assumption of an average B value, and not from exponential accentuation of experimental errors, as is the case for the complete extrapolated gum time procedure. For the simplified procedure, small experimental errors are not magnified on extrapolation; this renders this test more suitable for general use.

THEORETICAL CONSIDERATIONS

The simplified test variables, temperature and time, were left flexible in order to permit evaluation of the storage stability of all gasolines, which may vary from a few days to a few years. While the uncertainty in extrapolated gum time is decreased at lower accelerated test temperatures, the test time is correspondingly increased; hence a compromise must be effected.

An uncertainty factor, UF, arises on extrapolation because of use of an average B value; this increases with increase in ΔB (difference between assumed and actual B value) and the extent of extrapolation. The UF may be defined mathematically as follows:

$$\log UF = \Delta B\left(\frac{1}{T_{ex}} - \frac{1}{T_{ac}}\right) \tag{3}$$

where UF = uncertainty factor in extrapolation
T_{ex} and T_{ac} = temperatures, ° K., of extrapolation and of accelerated test
ΔB = difference between assumed and actual B value, always taken as positive

At a given temperature, the true storage life is equal to the extrapolated storage life multiplied or divided by the uncertainty factor, UF, depending on whether the assumed B value was larger or smaller than the true B value. The uncertainty factor can also be expressed in terms of a possible deviation in storage temperature for a constant predicted storage life, as shown in Figure 2.

The extent of extrapolation, or magnification factor, MF, may be expressed as the ratio of times at the extrapolated temperature versus the accelerated temperature. It has been found convenient to express the times at extrapolated temperatures in months and those at accelerated temperatures in days. Using these units, the magnification factor may be defined as follows:

$$\log MF = B\left(\frac{1}{T_{ex}} - \frac{1}{T_{ac}}\right) - 1.4829 \tag{4}$$

where

$MF = \dfrac{\text{months of storage at extrapolated temperature}}{\text{days of storage at accelerated temperature}}$
T_{ex} and T_{ac} = temperatures, ° K., of extrapolation and of accelerated test
B = temperature coefficient

For a given B value, MF is a function only of the extent of extrapolation.

Figure 3 is a working nomograph derived from Equation 4 for the average B value of 5500, which relates magnification factors with accelerated and extrapolated (storage) temperatures.

By combining Equations 3 and 4, the uncertainty factor, UF, can be related with the magnification factor, MF, as follows:

$$\log UF = \frac{\Delta B}{B}(\log MF + 1.4829) \tag{5}$$

where all terms have the same meanings as for Equations 3 and 4. Thus, for a given B value, the UF increases both with an increase in ΔB or MF; this is shown graphically in Figure 4 for ΔB values of 250 and 500. These values of ΔB represent the probable and maximum uncertainty in B values for different gasolines that result from use of an average value. Figure 4 may be used therefore to ascertain the probable and maximum uncertainty associated with a given MF.

APPLICATION

Predicted storage times or temperatures can be determined from accelerated test measurements by use of the nomograph presented to Figure 3. The accelerating aging tests may represent a single aging time, which is indicative of the amount of gum formed after a given period of storage, or a complete gum time, which provides a prediction of the rate of gum formation in storage.

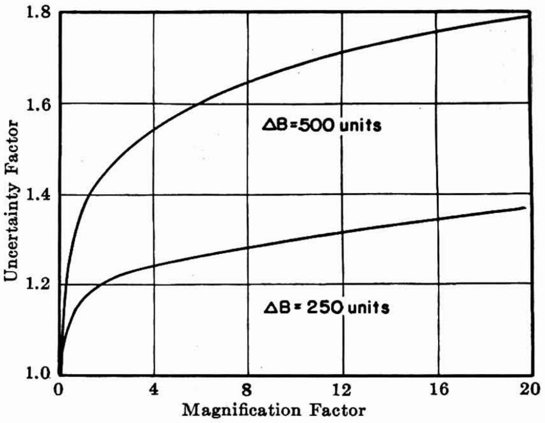

Figure 4. Relation between Magnification and Uncertainty Factor Resulting from Deviation between Assumed and Actual *B* Values

For single accelerated aging times, proper choice of test time and temperature will permit a prediction of the amount of gum to be expected in storage after a fixed time at a selected temperature. A complete accelerated gum time curve will permit a prediction of the rate of gum formation at any given storage temperature.

Table II. Summary of Calculated and Observed Gum Times Obtained under Varying Conditions for Two Gasolines

Aging Conditions	Stability Measurements		Gasoline A	Gasoline B
100° C., 100 p.s.i. oxygen pressure	Induction period, hours		5.25	1.08
	Initial A.S.T.M. gum, mg./100 ml.			
	Observed		0.6, 0.8	0.2, 0.2
	Extrapolated		0.25	0.1
	5 mg. A.S.T.M. gum time			
	Hours		3.47	0.90
	% of induction period		66.1	83.2
	Value of constant B (from Equation 1)		5790	5640
	Value of constant D (from Equation 2)		−0.110	−0.040
65.5° C., 1 atm. air	5 mg. A.S.T.M. gum time	Measured	6.8 days	......
		Calcd. from 100° C. measurements[a]	6.7 days	......
60° C., 1 atm. air		Measured	....	3.0 days
		Calcd. from 100° C. measurements[a]	....	2.5 days
90° F., 1 atm. air		Calcd. from 100° C. measurements[a]	13.1 mos.	2.7 mos.
		Calcd. from lower temperature measurements[b]	13.0 mos.	3.1 mos.

[a] Assuming B value of 5500 and indicated D value.
[b] Assuming B value of 5500; no pressure effect.

Table III. Pertinent Features of Different Type Bombs Used for Modified Stability Test Method

(Working pressure of all bombs, 50 pounds per square inch gage)

Container Size	Pint Bottle	Quart Bottle	0.5-Gallon Jug
Inside diameter, inches	3	$3\,^7/_8$	$5\,^1/_{16}$
Inside length, inches	$9\,^{15}/_{16}$	9	11
Wall thickness, inches	$^3/_{16}$	$^5/_{64}$	$^3/_{32}$
Total bomb volume, ml.	1170	1750	3610
Volume occupied by container, ml.	155	255	360
Volume available for gasoline and air, ml.	1015	1495	3250
Clearance between bomb and container, inches	$^1/_{32}$	$^1/_{16}$	$^1/_{32}$

Citing specific examples, a single aging time of 24 hours at 69.6° C. would be equivalent to 3 months' storage at 90° F. (see Figure 3). Likewise a 5-mg. gum time of 3 days at 73° C. would be equivalent to 6.3 months at 100° F. The probable uncertainty in the time or temperature predictions by either measurement could be determined by use of the nomograph (Figure 3) in conjunction with the temperature and time uncertainties presented in Figures 2 and 4.

TEST DEVELOPMENT

Equipment and Procedure. The bombs were made of low-carbon steel, cadmium-plated to prevent rusting, and built to withstand a working pressure of 50 pounds per square inch gage at test temperatures. No pressure gages or shutoff valves were required, since the bombs were opened and closed under atmospheric conditions. Several bombs, shown in Figure 5, were tested and found satisfactory. The pertinent features of these are given in Table III. The larger bombs were used for routine studies. The bombs were housed in an oil thermostat, Figure 6; temperature control was maintained on the order of ±0.1° C.

Studies were made of the temperature lag of the gasoline in the bomb on the basis of heating and cooling curves obtained under the exact operating conditions by means of a thermocouple passing through the bomb top. By use of a boiling water bath for preheating and an ice water bath for final cooling, the heating and cooling corrections could be eliminated without introducing error, provided the bombs were preheated for the specified times (for given test temperatures) shown in Table IV.

TEST PROCEDURE: The clean bottles are filled with the desired amount of gasoline, usually 750 ml., which has been precooled to about 5° C. A loose-fitting glass cap is placed over the neck and the bottle is immediately placed and sealed in the clean bomb. Care must be taken to prevent undue agitation prior to closure.

The sealed bomb is preheated in a boiling water bath for the prescribed time (Table IV). After preheating, the bomb is removed and placed in the thermostated bath which has been brought up previously to operating temperature. Oxidation is allowed to proceed for the desired length of time, following which the bomb is removed and plunged into a bucket of ice water for at least 15 minutes. The time of placement in the preheating bath is considered the start of the test, and the time of placement in the ice water bath is considered the completion of the oxidation time.

After cooling, the bomb is removed from the ice water and opened, and the sample is removed. If only a portion of the oxidized sample is to be used, the portion required is removed and the remainder is chilled, gently purged with air, and replaced in the recleaned bomb. In the latter event, the heating, operating, and cooling cycles are repeated a sufficient number of times to permit the determination of the rate of formation of gum as a function of time.

Reliability and Reproducibility. Comparable complete accelerated stability tests were made on two full-range cracked gasolines by the modified gum time and the extrapolated gum time methods. The procedure for the latter was given in another

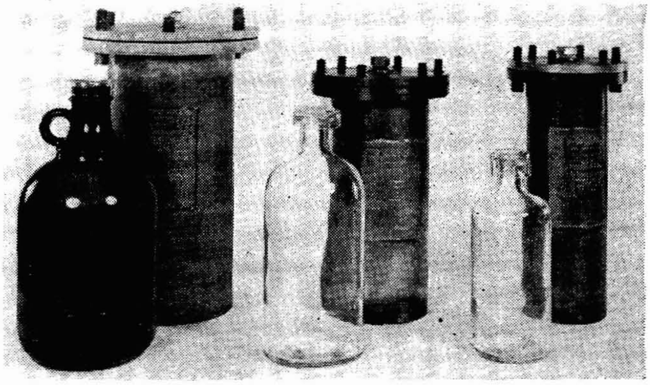

Figure 5. Simplified Aging Test Bombs

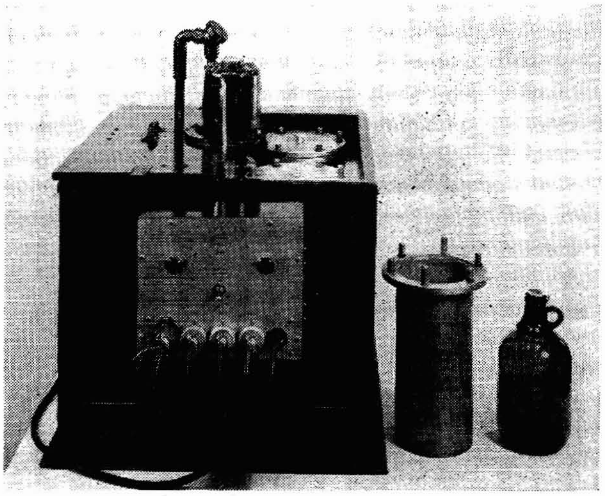

Figure 6. Simplified Test Apparatus

Table IV. Required Time of Preheating in a Boiling Water Bath for Various Final Oxidation Temperatures

Temperature of Oxidation, ° C.	Required Preheating Period, Minutes[a]
50	9
55	11
60	13
65	15
70	18
75	20
80	23

[a] Determined from time-temperature measurements of bomb contents.

paper (*3*). The agreement between the measured and predicted stability measurements by the two methods is good.

The reproducibility of the simplified testing procedure was checked by determining the complete gum curve for a given gasoline in each of four large bombs. Initially, each bomb contained 750 ml. of gasoline (air-to-gasoline volume ratio = 3.3), with 125-ml. portions being removed at varied intervals. The rate of gum formation *vs.* the time of aging is shown in Figure 7. The reproducibility is considered good, inasmuch as the data for all four samples fall along a smooth curve.

Influence of Operating Variables. In tests such as the above, the air-to-gasoline volume ratio varies as the test proceeds owing to removal of sample. The influence of this factor was evaluated by conducting tests with variable air-to-gasoline volume ratios in one bomb, and fixed but different ratios in three other bombs. The fixed conditions were attained by starting with fresh gasoline samples for each oxidation time. The results, summarized in Table V, show that gum times determined under these different air-to-gasoline volume ratios agree very well. It is accordingly indicated that the air-to-gasoline volume ratio need not be controlled closely as long as it falls within the range of about 3 to 25. Lower ratios than these should be avoided to prevent oxygen depletion effect (*3*).

Table V. Effects of Air-to-Gasoline Volume Ratio on Measured Rate of Gum Formation at 64.2° C. and 1 Atmosphere Air Pressure

(Total air plus gasoline volume of each bomb, 3250 ml.)

Volume of Gasoline in Bomb during Oxidation	Air-to-Gasoline Volume Ratio Maintained throughout Oxidation Period	Initial A.S.T.M. Gum		5 Mg. A.S.T.M Gum Time.
		Observed	Extrapolated	
Ml.		*Mg./100 ml.*		*Hours*
250	12.0			64.5
500	5.5			68.5
750	3.33	0.2, 0.4	0.27	68.0
Variable volume[a] (750–125)	Variable over range 3.33 to 25.0[a]			67.5

[a] Starting with 750 ml. of sample, 125-ml. portions were removed at various stages of oxidation and remainder further oxidized.

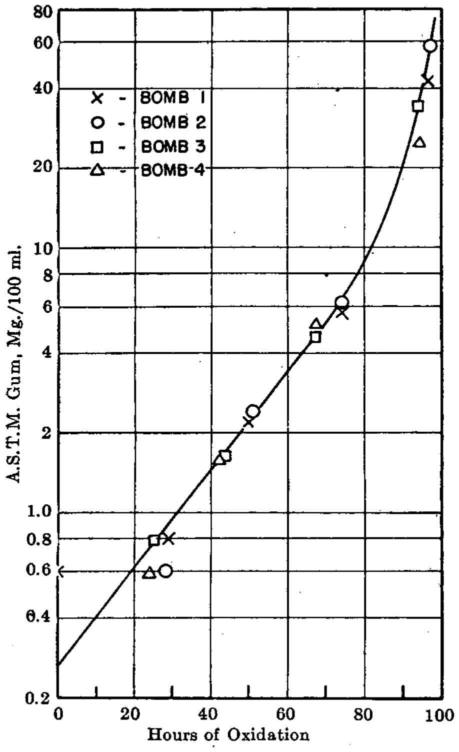

Figure 7. Reproducibility of Rates of Gum Formation under Simplified Test Conditions in Four Oxidation Bombs

Three sizes of bombs and glass liners are shown in Figure 5. Gum times were determined for a given gasoline in each bomb at a constant air-to-gasoline volume ratio—i.e., by introducing a fresh gasoline sample for each oxidation time. Table VI summarizes these data and shows that the gum times agree very well, indicating that bomb size is not an important factor.

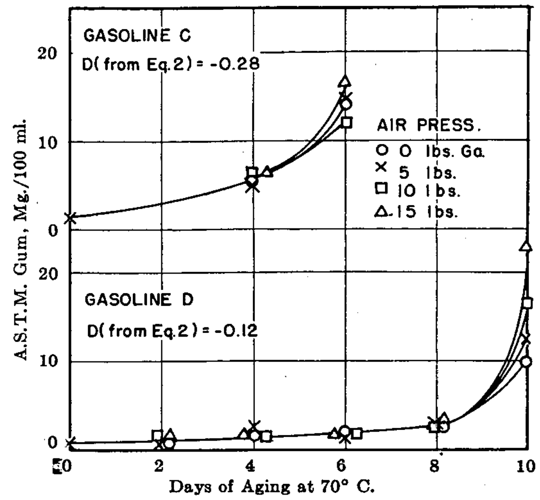

Figure 8. Effect of Small Air Pressures on Rate of Gum Formation

Table VI. Rates of Gum Formation at 64.2° C. and 1 Atmosphere Air for a Cracked Gasoline, Using Oxidation Bombs of Different Sizes

Size of Glass Container in Bomb	Bomb Volume	Gasoline Volume	Air-Gasoline Volume Ratio	Initial A.S.T.M. Gum		5 Mg. A.S.T.M. Gum Time
				Observed	Extrapolated	
	Ml.[a]	*Ml.*		*Mg./100 ml.*		*Hours*
Pint	975	200	3.88			89.5
Quart	1530	300	4.10	0, 0.2	0.12	92.5
0.5 gallon	3250	500	5.50			90.5

[a] Volume occupied by air plus gasoline.

GENERAL OBSERVATIONS

In general, this test has been found to be reproducible and to provide a reliable prediction of stability. Experience with different operators has shown that specific points requiring closest attention are the use of clean, dry apparatus and bomb equipment free of leaks. If leaks occur, the apparent stability of the gasoline will increase because of oxygen depletion effects. While this effect will not occur under normal operation, an added safety factor can be introduced by the use of small positive air pressures instead of atmospheric air pressure during the aging test. As shown in Figure 8, the accelerating effect of small air pressures is small, even for gasolines reasonably sensitive to oxygen pressure effects, and, when applied, can be neglected in stability predictions.

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Shale-Oil Naphthas

Analysis of Small Samples by the Silica Gel Adsorption Method

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A method for the analysis of small samples of shale-oil naphthas is based upon the selective adsorption of the various classes of compounds by silica gel. Data are presented on adsorbability of various classes of hydrocarbons, sulfur compounds, and nitrogen compounds. For best results, the tar acids and bases should be removed before analysis by this method.

THE synthetic liquid fuels program of the Bureau of Mines, as established by Public Law 290, 78th Congress, has as one of its objectives (*7*) the development of analytical methods suitable for the analysis of shale oil and its products. Naphtha from shale oil contains, in addition to paraffins, naphthenes and aromatics which are found in straight-run petroleum naphthas, large quantities of unsaturated hydrocarbons. Appreciable quantities of sulfur, nitrogen, and oxygen compounds are also present.

It was necessary in certain analytical studies to be able to determine the hydrocarbon groups in naphthas and fractions therefrom. The nature of shale oil limits the use of certain tests that are common in the petroleum industry. Bromine-number determinations for use in estimating the olefin content of shale oil are unreliable because of interfering substances. Specific dispersion or refractive-index determinations are made difficult by the color of the material, and methods for determining aromatics using these properties are subject to interference by olefin content. As limited quantities of the samples were available, a method was developed that utilized only 10 ml. of sample. This method was based upon the selective adsorption of the various classes of compounds by silica gel and was similar in principle to methods developed by the Bureau of Standards (*8–13*).

Treatment of shale-oil naphtha with sodium hydroxide solution (20% by weight) removes the so-called tar acids, which are largely phenolic in character. In different naphthas obtained from shale oils retorted by conventional methods from Colorado shales the quantity of this material ranges from 1.5 to 2%. The tar bases, which are removed by sulfuric acid (20% by weight), contain the major portion of the nitrogen compounds and generally comprise 5 to 7% of the naphtha, although in certain instances this figure has been as high as 15%. Removal of both tar acids and tar bases has little effect upon the sulfur content, which generally is slightly higher in the remaining oil than in the original naphtha, corresponding approximately to the volume reduction caused by the removal of tar acids and bases. For best results the tar acids and bases should be removed before analysis by this method.

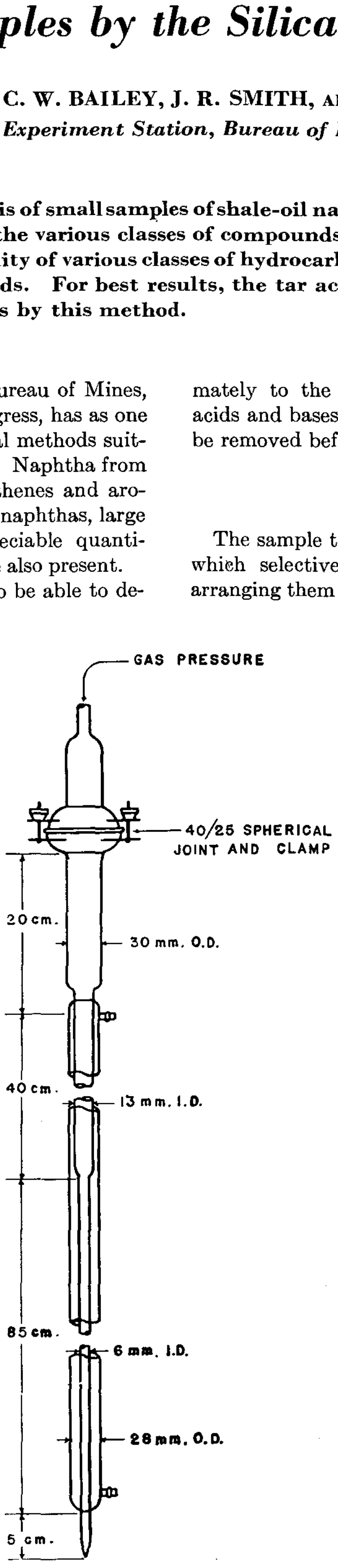

Figure 1. Apparatus Used for Analyses by the Silica Gel Adsorption Method

PRINCIPLE OF THE METHOD

The sample to be analyzed is passed into a column of silica gel which selectively adsorbs the various groups of compounds, arranging them in order of their decreasing adsorbabilities (*4, 14*). The sample is forced through the column by an appropriate desorbing liquid and collected in small fractions as it emerges. The refractive index (n_D) of each fraction is determined and plotted against the volume sum of desorbed sample to obtain an adsorptogram. [Recent developments in this field using continuous self-recording apparatus are discussed by Claesson (*5*)]. Although some of the fractions may be colored, it is usually possible to obtain the refractive index within the limits (±0.001) required by the method.

An adsorptogram consists of a series of plateaus (material of similar refractive index) separated by transition zones caused by mixing of compounds from the adjacent plateaus. It usually has three major plateaus corresponding to the following groups of compounds: (1) paraffins and naphthenes; (2) olefins; (3) aromatics, sulfur compounds, and such nitrogen compounds as may be desorbed. From a curve of this type, the percentage by volume of each of these groups may be calculated.

The adsorptogram sometimes may be used to calculate the volume percentage of subgroups when the separation of classes of compounds within a group gives an additional plateau on the curve or when proper corrections are made for the sulfur and nitrogen contents as determined by independent analyses. If the silica gel analysis is made on fractions of narrow-boiling range, so that relatively few compounds are present, the quantities of some of the individual compounds may be estimated when the adsorption results are used in conjunction with other data, such as ultraviolet absorption curves, density, and boiling range.

APPARATUS

The apparatus required for this analysis consists primarily of a silica gel column, as shown in Figure 1, and a refractometer capable of measuring the refractive index to ±0.001.

The present method was developed for use on samples containing a small volume of material, such as fractions obtained by distillation of shale-oil naphtha in an efficient fractionating column, so that no more than 10 ml. was available for the silica gel adsorption analysis. To provide for the size of sample, the column shown in Figure 1 was constructed. It is a modification of the column described by Mair (*8*); changes were made in the support provided for the silica gel, the manner of collecting samples, and the dimensions of the column.

The tip is drawn to a capillary (approximately 0.4 mm. in diameter), so that no fritted disk is required for support of the silica gel and remixing of the desorbed material as it leaves the column is eliminated as far as possible. This is an important factor in obtaining a sharp break between plateaus of the adsorptogram when small fractions are collected. As no provision is made for interrupting the flow, fractions must be collected continuously.

In order to reduce the size of the column, time required for an analysis, and handling loss, it is desirable to use the smallest quantity of silica gel that will give satisfactory separation of the groups of compounds. Several series of analyses were made on synthetic mixtures containing up to 90% olefins or 90% aromatics to determine this quantity. Satisfactory resolution of such mixtures was taken as an indication of the use of a sufficient quantity of gel. The procedure was to analyze several samples of a given synthetic mixture, using an increased quantity of gel for each successive sample until the components of the mixture were quantitatively recovered. Samples of a shale-oil naphtha were also analyzed, using quantities of silica gel ranging from 25 to 70 grams, until an increase of gel made no significant differences in the character of the curve obtained from the analysis. Figure 2 exemplifies the procedure; a shale-oil naphtha distilled from shale oil obtained from a Pumpherston retort was used in this test. Curves obtained on this sample with more than 50 grams of gel were essentially the same as that shown in Figure 2,*B*. From the results of these series of analyses it was concluded that a minimum of 50 grams of silica gel was necessary for a satisfactory analysis.

The adsorbent used in the work was silica gel (No. 22-08-05-01) manufactured by the Davison Chemical Corporation. A screen analysis of this material showed the following particle-size distribution: passing U. S. standard sieve No. 150, 85.7%; No. 200, 12.2%; No. 325, 1.7%. This material is coarser than that recommended by Mair (*8*). However, in the specified column the transition from one plateau to the next is generally accomplished in one to three fractions, which is a satisfactorily sharp break.

PROCEDURE

To prepare the column for an analysis a few grains of coarse silica gel, 28- to 200-mesh, are placed in the tip to support the finer material and to prevent clogging and 50 grams of silica gel of particle size comparable to that shown above are added. The column is then tapped gently for several minutes with a rubber-covered rod to pack the silica gel. Cooling water is run through the jacket on the column to dissipate the heat of adsorption.

A 10-ml. sample is introduced into the reservoir by means of a pipet. The reservoir is closed, and a pressure of 2 pounds per square inch (0.14 kg. per sq. cm.) gage is applied, using an inert gas, until all the sample has entered the silica gel. The pressure is released, and a few grams of silica gel are added to the reservoir to prevent the desorbing liquid from mixing with the sample. The reservoir is then filled with an appropriate desorbing liquid (2-propanol for samples boiling below 200° C.), and a pressure of 10 pounds per square inch (0.70 kg. per sq. cm.) gage is applied for the remainder of the analysis. When the sample begins to emerge from the column, fractions containing approximately 0.15 ml. each are collected in small test tubes. A volume of 0.15 ml. was selected because this is the smallest sample on which the refractive index may be determined conveniently. As it is difficult to measure such a small volume, the method used for determining the volume is to count the drops emerging from the column. The test tube used as a receiver is changed quickly when the volume (usually 8 to 12 drops) reaches 0.15 ml. The number of drops may be determined easily for any particular column by observing the number required to fill 3 ml.

The time required for a sample to pass through the column is about 2.5 hours. During the first hour the liquid reaches the bottom of the column, and in the remaining time the 65 to 70 fractions obtained in an average analysis are collected. The silica gel may be easily removed from the column in 15 to 30 minutes by inverting the column, attaching a rubber tube to the tip, filling this tube with acetone, and applying air pressure.

The refractive index of each fraction is determined and plotted against the volume sum of the desorbed sample, assuming that the volume of each fraction is exactly 0.15 ml. From this curve the per cent by volume of each group of compounds may be calculated. In this calculation the break between the groups of compounds is considered to occur between fractions showing the greatest difference in refractive indices. If two differences are approximately equal, the break is assumed to occur at the midpoint of the fraction between these differences. The break at the end of the curve, when determined as described, is assumed to represent a recovery of 100%. This is done to place all samples on a comparable basis, since the errors in determining the volume of the individual fractions are too great to permit use of the sum of the volumes as the true recovery. The volume per cent of a group of compounds is calculated by dividing the volume between adjacent breaks by the total volume of filtrate and multiplying by 100.

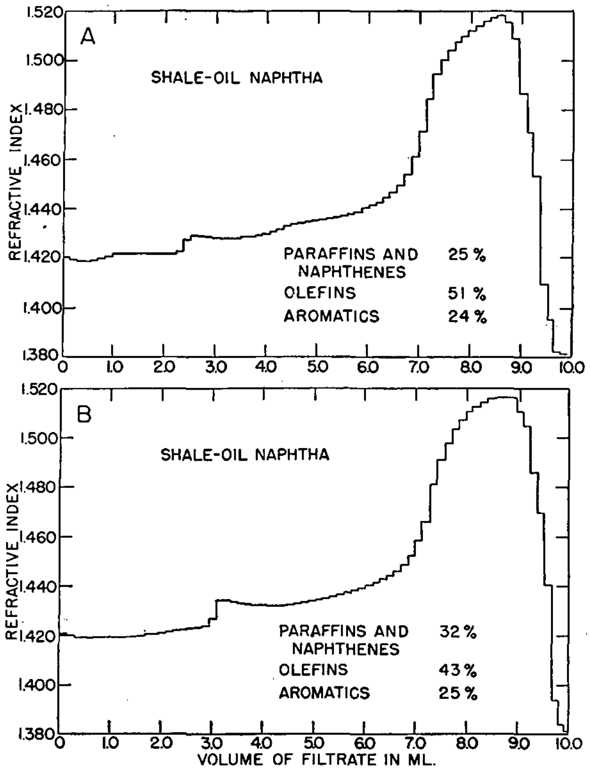

Figure 2. Analyses of a Shale-Oil Naphtha, Using Varying Quantities of Silica Gel

A. 35 grams B. 50 grams

An error is introduced if the loss of any compound is not in proportion to its original concentration, as, for example, if the sample contains materials that are more strongly adsorbed than the desorbing liquid and are consequently entirely lost in the analysis. An uncertainty also is introduced by the fact that the drop size varies for different types of compounds in the same boiling range. The size of the drops increases slightly in the order of paraffins and naphthenes, olefins, and aromatics. The volumes of the fractions are measured after separation of the components of the sample, introducing the additional variable of volume change due to mixing. These errors are not significant in routine use of the method, but they should be recognized and evaluated if more precise measurements are made to obtain better accuracy.

Another method for determining the volume of each group of compounds is to assume additivity of the refractive indices and apportion the fractions in the transition zone accordingly (*1*, *8*). Reference to the curves shown for synthetic mixtures indicates that this method is very satisfactory in such instances. However, in the analysis of complex samples from shale oil, where the transition zones are not sharp and the plateaus generally not flat, application of this system is difficult, if not actually impossible. Any increase in precision that might be obtained by this method dose not seem significant when the reproducibility of the method on actual samples is considered.

DISCUSSION

Separation of Paraffins and Naphthenes. In previous work the paraffins and naphthenes have generally been considered as one group, since any difference in adsorbability that exists between them is not sufficient to give a sharp separation. However, Mair and White (*11*) have reported that naphthenes are adsorbed in preference to paraffins and that individual paraffins are adsorbed in the order of decreasing molecular weight. These observations did not satisfactorily explain the curves obtained in the analysis of shale-oil fractions, as a decided decrease in refractive index and an extra plateau were often noted in the paraffin-naphthene portion of the curve. This suggested that the naphthenes were emerging from the column before the paraffins. Consequently, a series of analyses using synthetic mixtures was made to determine some of the factors governing the adsorbability of paraffins and naphthenes. The results indicate that the separation obtained is often due not so much to the character of the compounds as to their relative concentrations and molecular weights.

The effect of concentration is illustrated by the curves of Figure 3. The *n*-heptane and methylcyclohexane, which con-

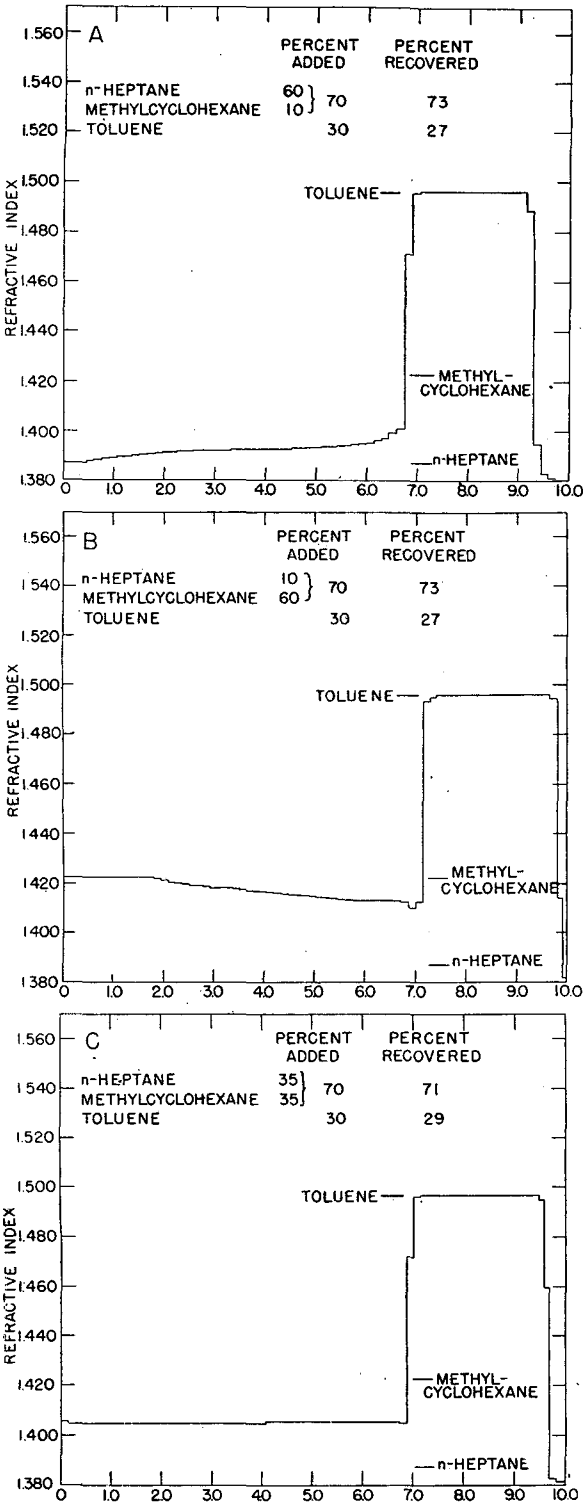

Figure 3. Effect of Relative Concentration on Adsorbability of Paraffins and Naphthenes

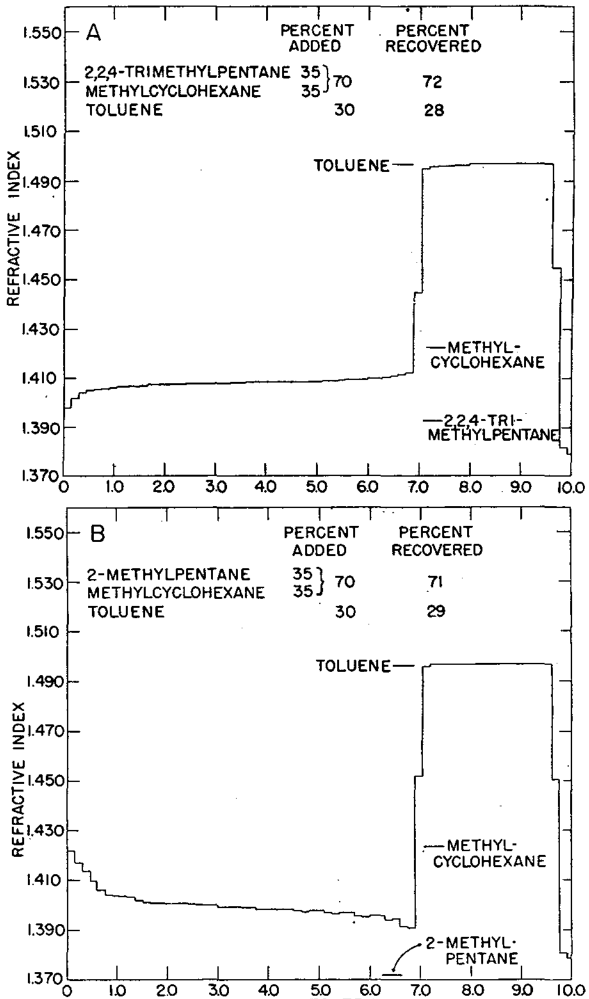

Figure 4. Effect of Molecular Weight on Adsorbability of Paraffins and Naphthenes

stitute the paraffin-naphthene portion of the sample for all three analyses, have the same number of carbon atoms and are consequently of approximately equal molecular weight, so that the variations in the curves appear to be due to the differences in concentration. It is evident that the compound of greater relative concentration tends to emerge from the column first, as the curve starts at virtually the refractive index of that compound (Figure 3, *A* and *B*). When the concentrations are equal, there is no apparent separation (Figure 3,*C*).

The effect of a small difference in molecular weight is shown by the analyses of mixtures of methylcyclohexane with 2,2,4-trimethylpentane and 2-methylpentane, respectively (Figure 4). The latter two compounds have, respectively, 1 more and 1 less carbon atom than the methylcyclohexane. An analysis was made using equal quantities of *n*-octane and methylcyclohexane and the results obtained were similar to those obtained using the branched-chain isomer of octane. While the presence of branched chains has some effect, that of molecular weight is predominant. The results of these analyses indicate that when a naphthene and a paraffin are present in equal concentration the compound containing the greater number of carbon atoms tends to issue from the column first, regardless of whether it is a paraffin or a naphthene.

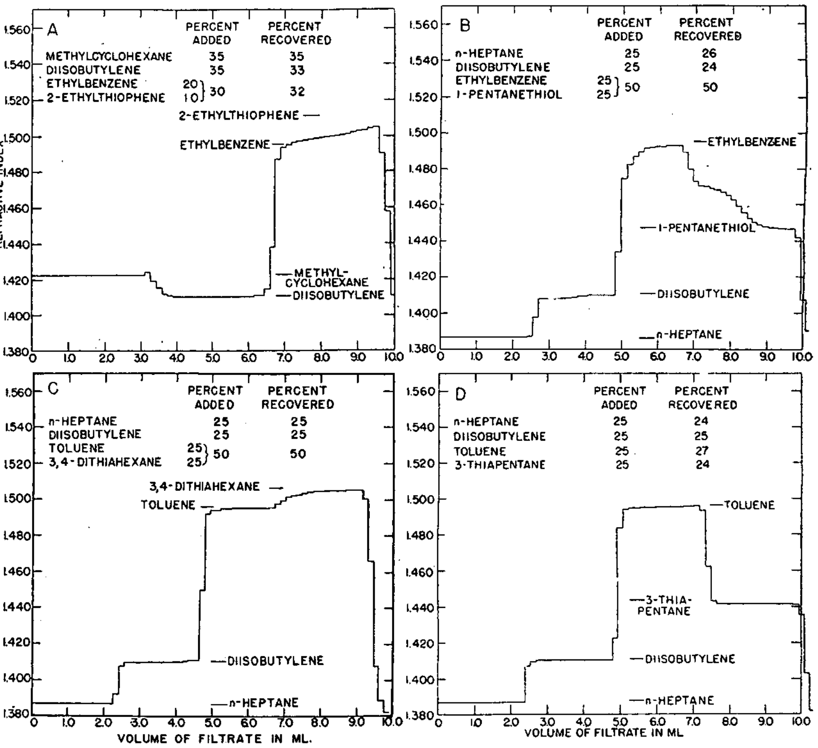

Figure 5. Analyses of Mixtures Containing Sulfur Compounds

Increasing the amount of methylcyclohexane until its concentration relative to the 2,2,4-trimethylpentane is 5 to 1 balances the effect of molecular weight, so that no separation of the two compounds occurs. However, if the difference in molecular weight is large, it cannot be overcome by altering the concentration within practical limits so that the high-molecular-weight material will tend to emerge from the column first.

Separation of Aliphatic and Cyclic Olefins. The aliphatic mono-olefins are more strongly adsorbed than the paraffin-naphthene group; this group of compounds therefore forms the next plateau on the curve. For this group the individual compounds also emerge from the column in the order of decreasing molecular weight, and the refractive index of the plateau frequently decreases from left to right.

The aliphatic mono-olefins are followed by the cyclic mono-olefins. The only cyclic olefin used in this work was cyclohexene, so that no results have been obtained concerning the effect of molecular weight on the separation between aliphatic and cyclic olefins. The break observed between cyclohexene and various aliphatic mono-olefins is sharp, suggesting that variations in adsorbability caused by molecular-weight differences could not reverse the order of emergence from the column. This conclusion is substantiated by the shape of curves obtained in the analysis of shale-oil fractions, although the difference in adsorbability is not usually sufficient to cause a sharp break between aliphatic and cyclic mono-olefins.

Separation of Aromatic, Sulfur, and Nitrogen Compounds. The last group of compounds to emerge from the column contains the aromatic hydrocarbons, sulfur compounds, and any nitrogen compounds whose adsorbability is less than that of the desorbing liquid.

The naphtha from shale oil contains a relatively large quantity of sulfur compounds. In order to interpret analytical results and make the proper corrections for these compounds it is necessary to know their effect on the adsorption analysis (*3*, *15*). A correction for sulfur compounds proposed by Mair (*8*) is based on the average refractive index of the sulfur compounds likely to be present in the gasoline range. This is satisfactory in the analysis of petroleum naphthas or when the quantity of sulfur compounds is so small that it is included without detection in the aromatics. However, in the analysis of shale-oil naphtha fractions, which may contain up to 15% of sulfur compounds, the aromatic portion of the curve is often considerably modified by these compounds. Several synthetic mixtures containing various sulfur compounds have been analyzed. The results of these analyses indicate that sulfur compounds are more strongly adsorbed than the aromatics occurring in shale-oil naphtha. The differences in adsorbability between the classes of sulfur compounds, while appreciable, are not as great as those between the various groups of hydrocarbons. In the analysis of shale-oil naphtha the actual separation obtainable between the sulfur compounds and aromatics depends on such factors as concentration and molecular weight in addition to the differences in adsorbability.

Thiophene and its derivatives are only slightly more strongly adsorbed than the aromatics of corresponding boiling range, so that the aromatic plateau slopes gradually upward but never closely approaches the value for the particular thiophene derivative present (Figure 5,*A*).

The difference in adsorption between thiols and aromatics and disulfides and aromatics is sufficiently great to give a distinct plateau at the refractive index of the sulfur compound present (Figure 5, *B* and *C*), although the break is not particularly sharp.

Sulfides, both aliphatic, such as 3-thiapentane (ethyl sulfide), and cyclic, such as 2-methylthiacyclopentane (2-methyltetrahydrothiophene), are so strongly adsorbed that the separation between the sulfide and the aromatic is as sharp as the breaks between the various groups of hydrocarbons. The quantity of sulfide may be estimated from the curve (Figure 5,*D*).

The correction to be applied for sulfur compounds is obtained by the equation:

$$V_s = \frac{P_s M D_f}{32 D_s}$$

where V_s is the volume per cent of sulfur compounds, P_s is the weight percent of sulfur, M is the average molecular weight of the sulfur compounds in the boiling range of the fraction being analyzed, D_f is the density of the fraction at 20° C., 32 is the atomic weight of sulfur, and D_s is the average density of the sulfur compounds at 20° C. The sulfur content is determined on a separate portion of the fraction. The percentage of sulfur compounds calculated by this equation is subtracted from the total percentage of aromatics obtained from the silica gel adsorption curve. This equation assumes 1 atom of sulfur to the molecule. An approximation for this correction, which is usually sufficiently accurate, may be made by omitting the densities in the above equation. Occasionally a check on the correction may be obtained when the curve shows a separate plateau attributable to sulfur compounds at the end of the aromatic group.

Synthetic samples containing representative compounds from several classes of nitrogen compounds, such as pyrroles, pyridines, and piperidines, were analyzed to determine the relative adsorbability of the nitrogen compounds. Pyrroles are more strongly adsorbed than any of the sulfur compounds used, but their adsorbability is enough less than that of the desorbing liquid to permit them to be recovered (Figure 6,*A*). The pyrrole used in this analysis was not purified, which may account for the large loss. The pyridines and piperidines are so strongly adsorbed that they do not appear in the filtrate, even though a number of fractions are taken after essentially pure desorbing liquid has been obtained (Figure 6,*B*). They do, of course, move down the column in accordance with chromatographic theory and would eventually issue from the tip. However, they are shown as a loss by this method of analysis.

The more basic compounds (tar bases), which are usually removed by an acid wash, are the ones most strongly adsorbed. Consequently, in a sample that has been so treated only the less strongly adsorbed compounds, such as pyrroles, are likely to

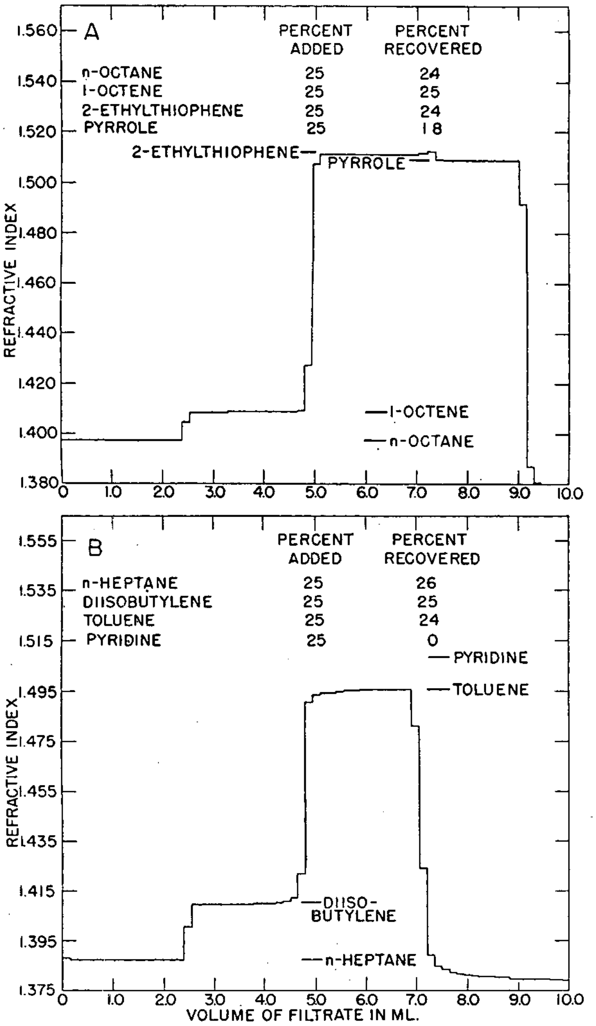

Figure 6. Analyses of Mixtures Containing Nitrogen Compounds

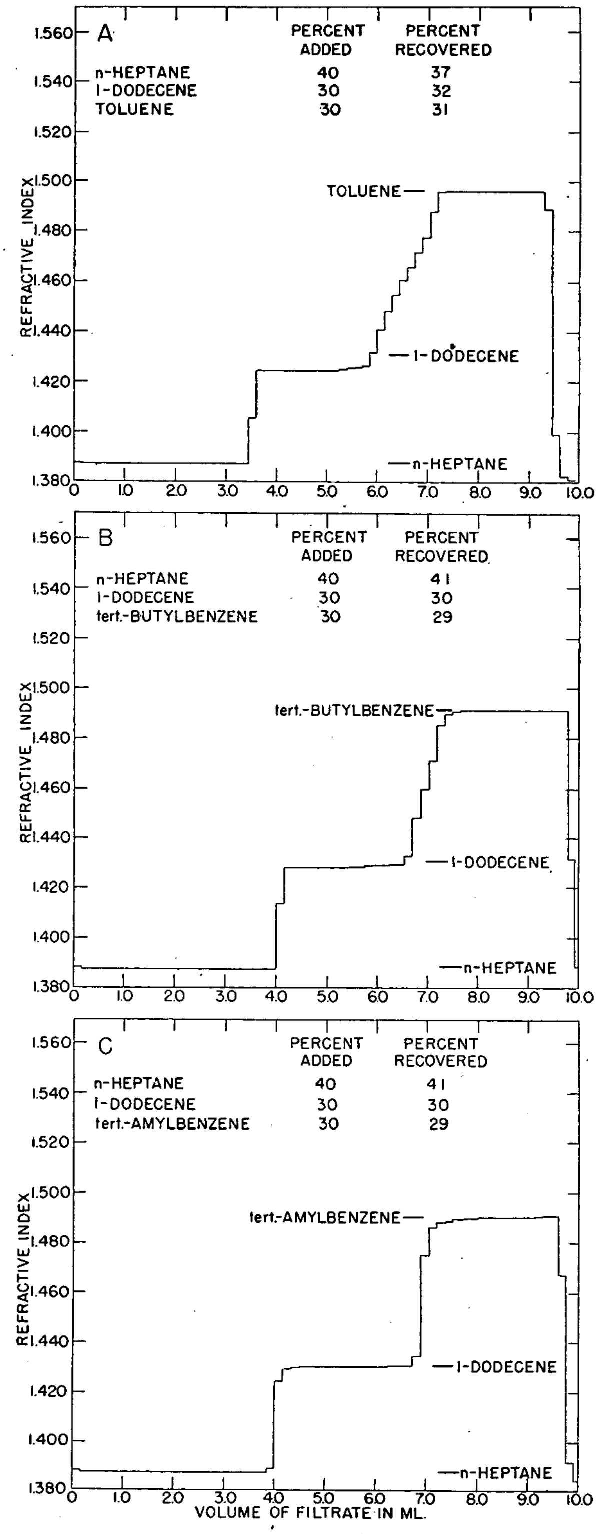

Figure 7. Effect of Viscosity

be present, and the correction can be made in the same manner as for sulfur compounds.

Effect of Boiling Range and Viscosity. The presence of constituents with low boiling points (below approximately 60° C.) caused marked fluctuations in the refractive indices of the paraffin-naphthene plateau. Since these compounds are paraffins of low molecular weight, they tend to appear at the end of this portion of the curve immediately before the olefin break and may cause difficulty in interpretation. The elimination of these compounds by distillation considerably simplifies the analysis.

Gooding and Hopkins (*6*) have shown that for silica gel adsorption work on higher-boiling petroleum distillates the viscosity of the desorbent must be higher than that of the material being desorbed. Experiments described in this paper have shown that viscosity is a factor not only for the desorbent but also for the groups that must be desorbed successively within a sample. When the aromatic group has a lower viscosity than either the paraffin-naphthene or olefin groups, difficulty is experienced in the analysis, as shown in Figure 7 where toluene does not desorb 1-dodecene quantitatively. However, *tert*-butylbenzene improves the analysis and *tert*-amylbenzene gives a satisfactory analysis.

The difficulty due to viscosity may be suspected when a very gradual break is obtained between groups of compounds. It has been found that when a sample contains a paraffin-naphthene group having a higher viscosity than other groups dilution with *n*-heptane permits a satisfactory analysis.

EXAMPLES OF ANALYSES APPLIED TO SHALE-OIL NAPHTHA

Hydrogenation. The method has been used to follow the course of hydrogenation of shale-oil naphtha. In order to obtain complete hydrogenation at relatively low temperatures of the olefins in shale-oil naphtha, a series of runs was required. As the hydrogenations were carried out in small-scale batch equipment, it was desirable to withdraw a minimum amount of sample for analysis after each run of a series. The adsorption method was used, since the bromine number has not been applied successfully as a measure of the olefin content of shale-oil naphtha. The method has the advantage of giving additional information on the progress of hydrogenation, such as the extent of attack on the compounds forming the aromatic group. The original naphtha (Figure 8,*A*) used as a charge for these experiments was from shale oil obtained by retorting Colorado shale in a Parry retort. The extent of reaction on this naphtha at different stages of hydrogenation is shown in Figure 8, *B* and *C*. The reduction in the aromatic group as hydrogenation proceeds is apparently caused largely by the removal of sulfur.

The method has been incorporated in an analysis scheme used to differentiate between crude shale oils obtained from different conditions of retorting. It has been used to evaluate results of cracking experiments, continuous hydrogenation experiments, and treating experiments.

Fractionation. Analyses of two fractions from a distillation of shale-oil naphtha are shown in Figure 9, which also includes for reference a plot of boiling point versus refractive index for a number of compounds occurring in the appropriate boiling range. Interpretation of these analyses is based upon the results on synthetic mixtures, trends indicated in the analyses of the series of fractions from which these two were selected, and other analytical data obtained on the fractions. The curves shown were selected because they represent two types of adsorptogram frequently encountered and illustrate the practical application of several points mentioned in the discussion.

The paraffin-naphthene group of fraction A shows the downward trend in refractive index characteristic of a sample containing a high concentration of naphthenes relative to paraffins (approximately 7 to 1). Before this phase of the curve was investigated by using synthetic mixtures, the olefin content was determined on a separate portion of the fraction by the nitrogen tetroxide method (*2*) to make certain that the lowest plateau of the curve did not represent aliphatic olefin. The result checked well with the olefin content for fraction A given in Figure 9. Fraction B contains only a small quantity of naphthenes. The olefin portions of the curves for both fractions show a mixture of aliphatic and cyclic olefins; fraction A has a higher relative proportion of cyclics.

The aromatic portions of both curves indicate the presence of sulfur compounds of high refractive index. Although the quantity of sulfur compounds in each fraction is roughly the same, the concentration relative to the aromatics is more than twice as great in fraction A as in fraction B, so that the separation between the two classes in the former instance is relatively poor and the refractive index of the whole aromatic plateau is raised. In fraction B the separation is fairly good, and the refractive index of the major portion of the aromatic plateau corresponds to that of the xylenes.

From these silica gel adsorption curves, boiling-point data, ultraviolet absorption curves for distinguishing individual aromatics, and independent analyses for sulfur and nitrogen, an

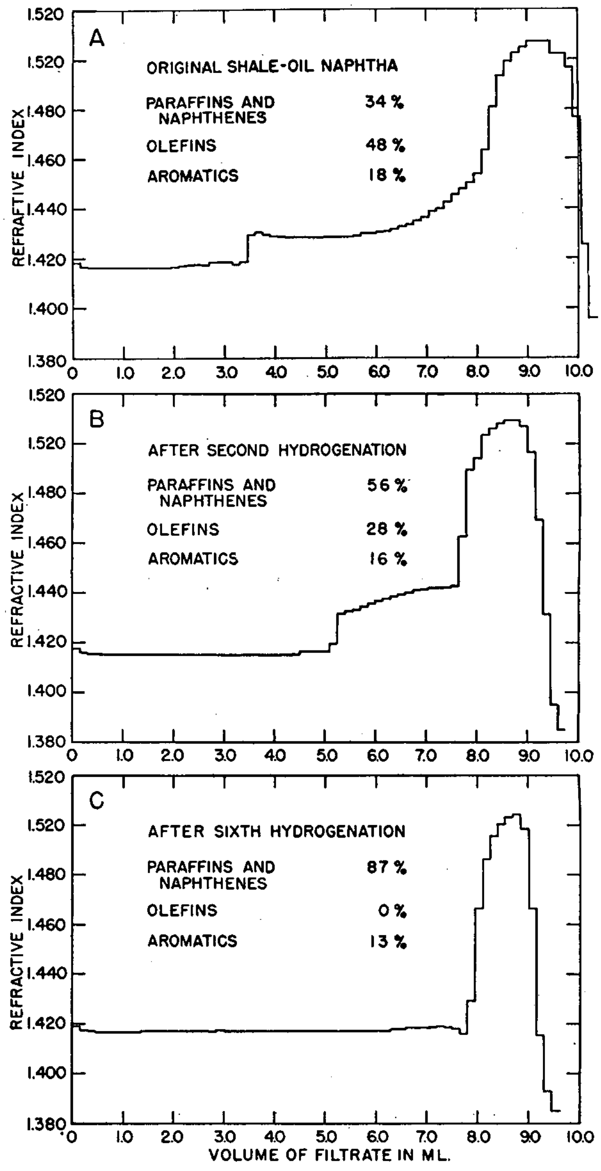

Figure 8. Analyses at Three Stages in the Hydrogenation of a Shale-Oil Naphtha

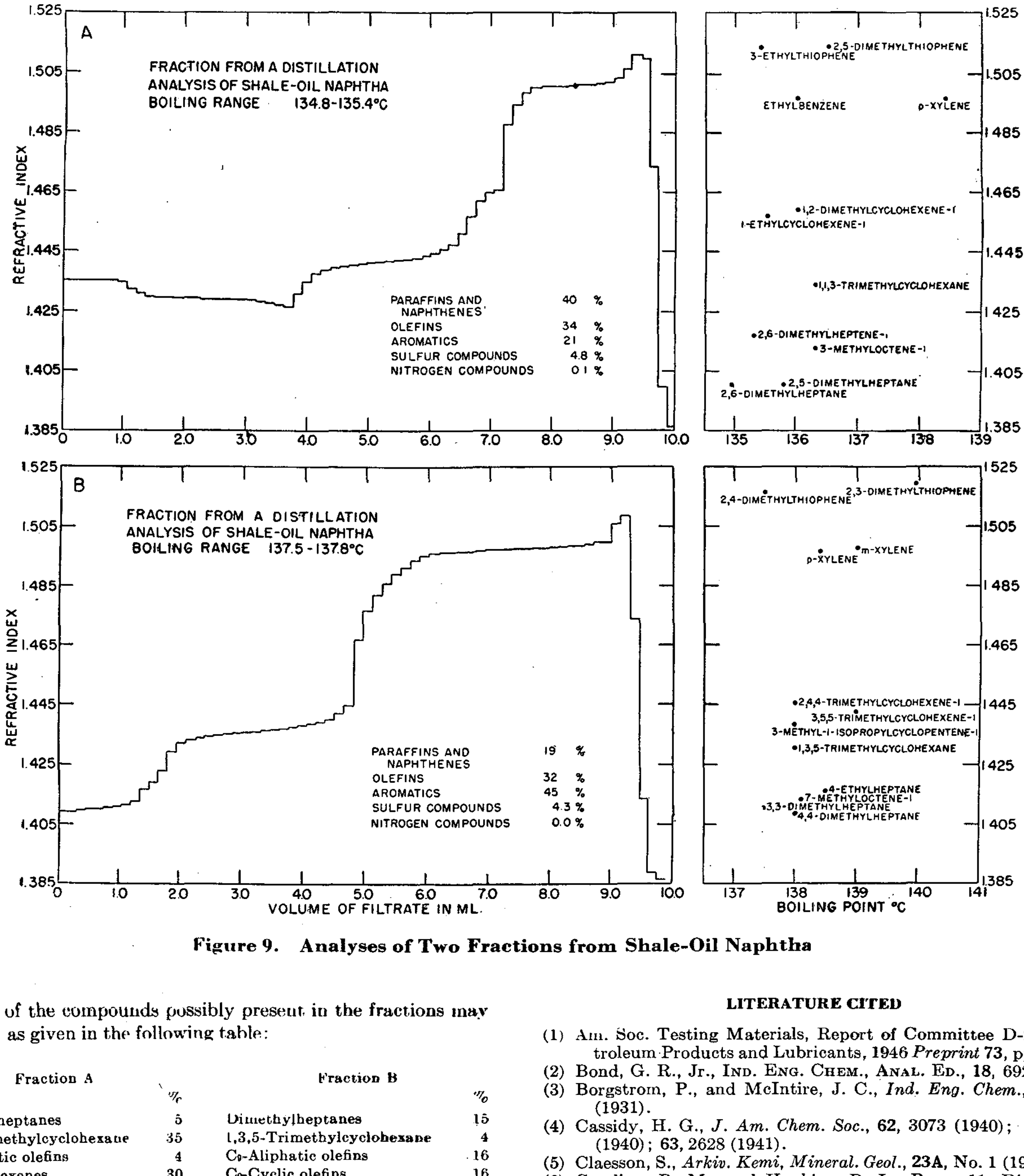

Figure 9. Analyses of Two Fractions from Shale-Oil Naphtha

estimate of the compounds possibly present in the fractions may be made, as given in the following table:

Fraction A	%	Fraction B	%
Dimethylheptanes	5	Dimethylheptanes	15
1,1,3-Trimethylcyclohexane	35	1,3,5-Trimethylcyclohexane	4
C_9-Aliphatic olefins	4	C_9-Aliphatic olefins	16
C_8-Cyclohexenes	30	C_9-Cyclic olefins	16
Ethylbenzene	10	*p*-Xylene	5
p-Xylene	11	*m*-Xylene	40
Thiophene derivatives	5	Thiophene derivatives	4

ACCURACY AND PRECISION

The method is more accurate when the concentrations of the various groups of compounds are approximately equal. Based on the determinations made on the known mixtures, the method is probably reliable for estimating certain components of shale oil with a possible error of 1 to 3%.

ACKNOWLEDGMENT

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Determination of Carbon Monoxide in Air by Use of Red Mercuric Oxide

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A new laboratory method for the determination of carbon monoxide in air makes use of the reaction: $CO(gas) + HgO(solid, red) = Hg(gas) + CO_2(gas)$. The gaseous sample is passed through a reaction tube containing granular red mercuric oxide held at a temperature of 175° to 200° C. The loss in weight of the reaction tube during passage of the sample is an exact measure of the quantity of carbon monoxide present and involves a highly advantageous gravimetric factor. The accuracy of the method has been demonstrated through the analysis of three unknowns submitted by the National Bureau of Standards.

THE determination of carbon monoxide has long been an important problem because of its frequency of occurrence and high toxicity. During the war the problem assumed even greater importance in connection with the design of aircraft and tanks.

The most widely used laboratory procedure for the determination of carbon monoxide involves reaction with iodine pentoxide. Much that is contradictory and controversial, has been written about this method, which is accurate only when used by a careful and skilled worker.

In the search for a more accurate and less tedious method for determination of carbon monoxide and one which might lend itself to instrumentation, the reaction with mercuric oxide was considered.

Fay and Seeker (*2*) stated that carbon monoxide is oxidized by yellow mercuric oxide at 0° C. and by the red oxide at 96° C. Moser and Schmidt (*4*) claimed that the red oxide showed little activity at 100° C. but did react at 160° C. They found the yellow oxide much more reactive and used it for analytical purposes at 100° C. At this temperature the reaction was shown to be complete with respect to the carbon dioxide formed at the flow rates they employed. Grigarjew (*3*) also used the yellow oxide at 100° C. and determined the carbon dioxide formed. None of these workers attempted to use red mercuric oxide for analytical purposes, probably because of its lower reactivity.

Yellow mercuric oxide appears to be an active but unstable material without definite physical properties—for example, Schoch (*6*) found the dissociation pressure of the yellow oxide to be higher than that of the red form and to decrease with time. Because of this lack of definite properties on the part of the yellow form, the red oxide which has a definite dissociation pressure–temperature relationship was given further consideration.

Thermodynamically the reaction between red mercuric oxide and carbon monoxide is favorable, as shown by the free-energy equations below:

$$\text{HgO (solid, red)} + \text{CO (gas, 1 atm.)} = \text{Hg (liquid)} + \text{CO}_2 \text{ (gas, 1 atm.)}, \ \Delta F_{298} = -47.5 \text{ kcal.} \quad (1)$$

$$\text{HgO (solid, red)} + \text{CO (gas, } p \text{ atm.)} = \text{Hg (gas, } p \text{ atm.)} + \text{CO}_2 \text{ (gas, } p \text{ atm.)} \quad (2)$$

$$\Delta F_{473} \ (p = 1 \text{ atm.}) = -50.0 \text{ kcal.}$$

$$\Delta F_{473} \ (p = 10^{-4} \text{ atm.}) = -58.6 \text{ kcal.}$$

The last conditions stated correspond closely to those used analytically.

The determination of carbon monoxide by means of mercuric oxide may be carried out in any one of three ways: The carbon dioxide resulting may be collected and titrated; the mercury vapor may be determined by an instrument to be described in a later communication; or the loss in weight of the reaction tube during passage of the sample may be observed. The last two procedures would be invalidated by any catalytic oxidation of carbon monoxide by oxygen of the air on the surface of the mercuric oxide or by appreciable dissociation of the oxide. The absence of catalytic oxidation is indicated by the fact that reliable results are obtained both by determination of mercury and by the loss in weight. The effect due to dissociation of mercuric oxide is discussed below in connection with the air blank.

The loss-in-weight procedure was found to give a convenient and accurate laboratory method for the determination of carbon monoxide in air. Since 28 mg. of carbon monoxide cause a loss of 216.6 mg., there is a highly advantageous gravimetric factor of 7.74. The loss in weight amounts to 0.968 mg. per liter (S.T.P.) of gas containing 100 p.p.m. of carbon monoxide.

APPARATUS AND PROCEDURE

Preparation of Granular Red Mercuric Oxide. Commercial red mercuric oxide is a dense powder which offers considerable resistance to the flow of gas and is so fine that it blows with the air stream, even when placed between tight plugs of glass wool. These difficulties were overcome by preparing a granular form of the oxide as described below.

About 50 to 100 grams of reagent grade (General Chemical Co.) mercuric nitrate are placed in an evaporating dish and heated over a Meker burner in a well-ventilated hood. During the early stages of the heating, the hydrate melts, loses water, and solidifies. At this time there is apt to be considerable spattering and the heating should be carried out cautiously. Further heating causes decomposition of the nitrate with liberation of oxides of nitrogen. After a few minutes of strong decomposition, the burner is removed and the dish allowed to cool. If the decomposition has progressed far enough, the mass may be easily removed from the dish. It is then broken up into small pieces but not powdered and is subjected to further strong heating. The bottom of the dish is kept near red heat and the mass is stirred occasionally with a glass rod. The material is dark brown at this stage while hot and there is usually considerable decomposition into mercury and oxygen. The material is cooled again, and the larger lumps are broken up. If any light-colored spots appear, the heating should be resumed until the lumps are orange-red throughout on cooling. The only danger involved in overheating is a greater tendency for the material to powder.

After decomposition is complete, the material is screened, and that accepted which passes the 8-mesh screen but is retained by the 14-mesh screen. The material larger than 8-mesh is gently broken up and subjected to further screening. The 8- to 14-mesh oxide is then baked out for 8 to 10 hours in a slow stream of pure, dust-free, and oil vapor–free air at 230° to 250° C. to remove free mercury. If compressed air is used for this purpose, a charcoal trap is recommended for removal of oil vapor.

Balance. A semimicrobalance manufactured by Ainsworth and Sons was employed. Weighings could be made to 0.01 mg. but in practice the reproducibility of the wiping and weighing technique was 0.04 mg.

Reaction Tube. The reaction tube is shown in Figure 1. The main body is made of 9-mm. Pyrex tubing, while the ends are of 5-mm. tubing. The constrictions aid in reducing diffusion of moisture into the tube during weighings. Pyrex glass wool is used for plugs. The weight of the unit is 17 grams, about 8 grams of which are mercuric oxide.

Furnace. The furnace consists of a horizontal copper pipe 3.75 cm. (1.5 inches) in diameter by 24 cm. (8 inches) long, heated by means of a Nichrome coil. The desired temperature is obtained by regulation of the applied voltage through a variable transformer. The copper pipe with its heating coil is mounted in a can 10 × 10 × 20 cm. (4 × 4 × 8 inches) and insulated with glass wool. The ends of the pipe are fitted with Transite plugs, the front one being removable, so that the reaction tube may be inserted or taken out. The reaction tube is held in place by this plug at the front end and by a Nichrome support at the rear end. A thermometer is inserted in the furnace with the bulb just above the center of the reaction tube.

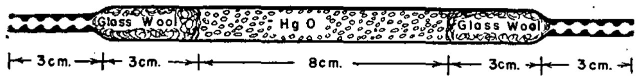

Figure 1. Reaction Tube

Gasometer. The sample to be analyzed is collected in the gasometer shown in Figure 2. The gasometer consists of a 7-liter bottle, a water-level indicator, and a 19-liter (5-gallon) bottle which serves as the upper reservoir. Since the gas sample is always under a pressure greater than atmospheric, it is necessary to have both ends of the level indicator communicate with the bottle as shown. The gasometer was calibrated at 500-ml. intervals by use of a volumetric flask. A calibration curve was then made for the level indicator and it was possible to make readings of the level to an accuracy of 0.3 mm., which corresponds to 8 ml. in the bottle. The air space in the upper reservoir ordinarily communicates with the atmosphere. By applying suction to the upper reservoir it is possible to draw a sample into the gasometer preliminary to its analysis. Usually, however, the sample was contained in a tank and could be delivered into the gasometer under its own pressure. After the system comes to rest, the pressure of the gas in the gasometer is computed from the barometric pressure, the difference in the two water levels, and the partial pressure of the water vapor in the sample, assuming the sample to be saturated at the laboratory temperature.

Arrangement of Apparatus. The general arrangement of the apparatus is shown in Figure 3. The drying tubes and charcoal trap are of a large size, 2.5 × 20 cm. (1 × 8 inches) for increased effectiveness and longer life. The trap is filled with a good grade of activated charcoal. Columbia 6G ground to 8- to 14-mesh was found very effective in the removal of certain interfering substances mentioned below.

Conditioning Reaction Tube. Before making analyses, the mercuric oxide should be conditioned in a stream of pure, dry air, first at 250° C. for several hours, then for an hour or two at 200° C., the usual reaction temperature. A flow rate of 200 to 300 ml. per minute is suitable for this flushing.

Wiping and Weighing Procedure. In order to obtain successive weighings which are reproducible to a few hundreths of a milligram, the tube must be brought to some standardized state of moistness with respect to adsorbed water. Wiping techniques described by Niederl and Niederl (*5*) aid in obtaining reproducibility.

The tube is first wiped over its outer surface with a wet (but not dripping) cloth. It is next wiped with a damp chamois, and finally a careful wiping is made using a chamois which is in equilibrium with the moisture in the balance case. During each step in the wiping, two pieces of cloth or chamois are used, the tube being held firmly near one end by one piece while wiping with the other. Ends are interchanged once during each step in the wiping. Care is taken not to introduce water into the open ends of the tube.

The tube is then placed on a Nichrome rack in the balance case and exposed for 5 or 6 minutes to the light from a quartz mercury arc to remove the electrostatic charges induced in the final wiping. The actual weighing is performed 10 minutes ± 15 seconds from the time of completion of the final wiping. With the balance employed, the wiping and weighing sequence could be carried out repeatedly with a reproducibility of 0.04 mg. This wiping and weighing procedure should be practiced a number of times before attempting analytical work.

The timing of the wiping and weighing is important and variations should be kept within 15 seconds. The exposure to ultraviolet light is indispensable when the relative humidity is below 50% and is recommended as a standard part of the procedure. Other means for removing electrostatic charges are sometimes recommended but in the opinion of the authors the ultraviolet lamp is best. A hot arc should not be used because of its heat effect.

Analytical Procedure. Bring the furnace to the desired operating temperature. A temperature of 200° C. is recommended if no interfering substances are present. When hydrogen is present, the reaction temperature should be dropped to 175° C.

Fill the gasometer with the sample to be analyzed.

Flush the line including the reaction tube with about 600 ml. of the sample.

Remove the reaction tube from the furnace, placing it on a Nichrome rack. Cool for 20 minutes in the open air.

Wipe the tube, expose to ultraviolet light, and weigh as described above.

Replace the tube in the furnace and allow 15 to 20 minutes for it to reach operating temperature.

Record the water level in the gasometer, the difference between the water levels in the upper and lower reservoirs, the barometric pressure, and the temperature.

Start the gas flowing using a rate of about 100 to 200 ml. per minute. Permit about 5 liters of sample to pass.

Stop flow of gas. Remove reaction tube. Record gasometer reading, temperature, and difference in water levels.

Cool, wipe, and weigh tube as before.

DISCUSSION

Sources of Error. The principal sources of error are those affecting the determination of the volume of the gas sample, those affecting the determination of the loss in weight, and the air blank.

VOLUME MEASUREMENT ERRORS. The gasometer volume can be read within 8 ml., so that the total error from this source could be 16 ml. Since a sample of about 5 liters is usually measured, this error could amount to about 0.3%. Calibration errors in the

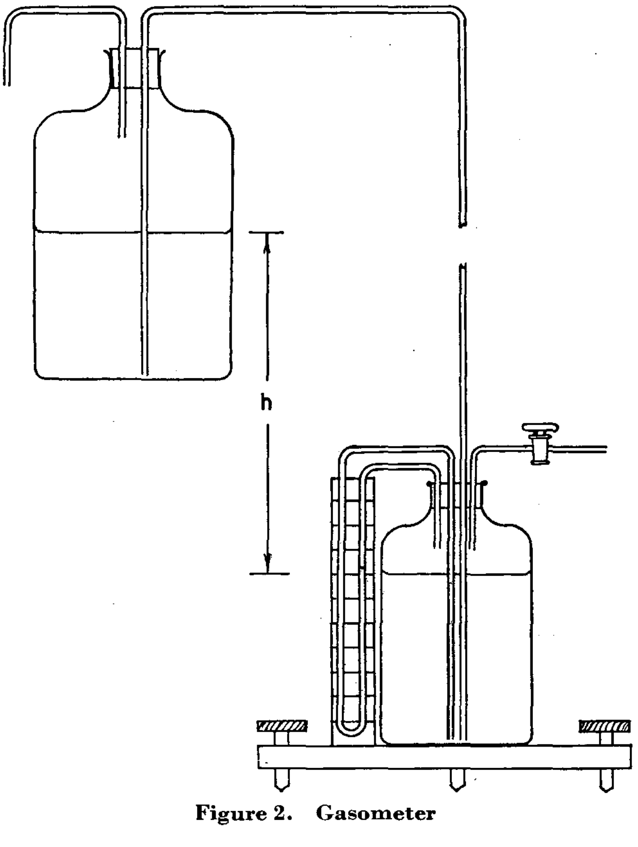

Figure 2. Gasometer

gasometer are probably no greater than 0.1%, while errors in measurement of temperature and pressure may contribute 0.1%. The maximum possible error in the measured volume of the sample would accordingly appear to be 0.5%.

WEIGHING ERRORS. Experiments showed that the weighings were reproducible to within 0.04 mg. This might lead to an error as high as 0.08 mg. in the measurement of the loss in weight in a given determination. Since the loss in weight varies with the carbon monoxide concentration, the per cent error will also vary, being about 1.2% at 100 p.p.m. where the weight loss is about 0.0065 gram and about 0.3% at 400 p.p.m. where the loss is about 0.0260 gram.

The reproducibility expected for carbon monoxide determinations is thus within 1.7% of the mean value at concentrations around 100 p.p.m. and 0.8% at concentrations around 400 p.p.m. In p.p.m. these limits are 1.7 at 100 p.p.m. and 3.2 at 400 p.p.m. Nearly all the results shown in Table III show deviations from the mean which are within the above limits.

THE AIR BLANK. When pure, carbon monoxide–free air is passed over red mercuric oxide at 175° to 200° C. there is a loss in weight. This is to be expected, since the oxide has an appreciable dissociation pressure at this temperature. The dissociation pressure of red mercuric oxide is 3.0×10^{-4} atmosphere or 0.228 mm. at 200° C.; hence if the oxide were to come to equilibrium with oxygen at its partial pressure in the air, the resulting air would contain 4 p.p.m. (by volume) of mercury. Experimental values for the air blank are in good agreement with this value, as shown by the data in Table I.

Determinations 1 to 4 were made using laboratory air. Since there may have been some carbon monoxide in the laboratory air, determinations 5 and 6 were made using air which was certain to be carbon monoxide–free. Absence of carbon monoxide was assured by passing the laboratory air through a train consisting of a tube containing red mercuric oxide at 200° C., a second tube containing solid iodine to remove mercury vapor introduced by the first tube, and a third tube containing activated charcoal to remove iodine vapor.

The values given are for carbon monoxide–free air. When the sample contains carbon monoxide, the air blank generally is less than 4 p.p.m. The analysis of standard samples shows that the air blank falls off with rising carbon monoxide concentration, reaching a minimum value of 1 p.p.m. at a carbon monoxide concentration of about 100 p.p.m., after which it rises. A correction of −1.0% is indicated for the range from 100 to 400 p.p.m.

Effect of Temperature on Completeness of Reaction. Although the reaction between carbon monoxide and red mercuric oxide is thermodynamically favorable even at 25° C., the reaction rate is too slow at low temperatures to permit quantitative work. Using flow rates and reaction tube dimensions approximately as previously given, the completeness of reaction as a function of temperature was studied with the results shown in Table II.

Effect of Flow Rate on Completeness of Reaction. At 200° C. the analytical results showed fluctuations of about the magnitude indicated in the discussion of the sources of error when flow rates of 50, 100, and 200 ml. per minute were employed. However, two determinations made at 500 ml. per minute on a sample containing 293 p.p.m. gave results 5 and 4% low, respectively, indicating too rapid a flow. Although no complete study was made at lower temperatures, the reaction was found to be substantially complete at a flow rate of 200 ml. per minute at 175° C.

Table I. Loss in Weight of Red Mercuric Oxide in Pure Air at 200° C.

Determination No.	Carbon Monoxide P.p.m.
1	2.1
2	4.5
3	4.5
4	3.9
5	4.0
6	4.0
Av. (omitting 1)	4.2

Table II. Completeness of Reaction between Carbon Monoxide and Red Mercuric Oxide as a Function of Temperature

(Carbon monoxide concentration, approximately 200 p.p.m.)

Temperature, ° C.	% Completion
125	4
146	62
167	90
175	98
200	100

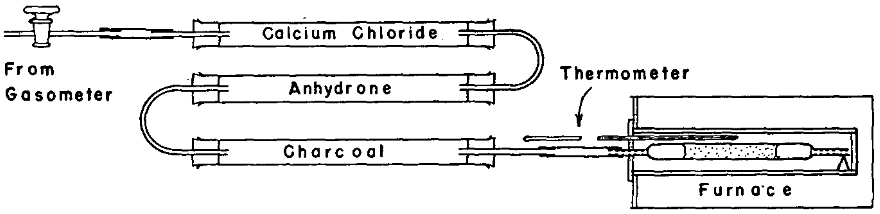

Figure 3. Arrangement of Apparatus

Effects of Other Reducing Gases. The effects of hydrogen, methane, butane, ethylene, pentene, benzene, and chlorobenzene on mercuric oxide at 175° to 200° C. were studied. The details of this study are to be found in the final report (*1*) to the Office of Scientific Research and Development and only a summary is given here. Unless otherwise specified, the conditions are those described in the analytical procedure.

Hydrogen reacts to the extent of 50% of its true concentration at 200° C. but only to the extent of 5% at 175° C. Hence the temperature should be kept near 175° if hydrogen is present.

Methane does not react.

Higher saturated hydrocarbons are reactive, the reactivity increasing with molecular weight. A good activated charcoal trap removes these materials.

Unsaturated hydrocarbons react but are also effectively removed by the activated charcoal trap.

Aromatic compounds exhibit a strong poisoning effect which renders the mercuric oxide inactive toward carbon monoxide. The poisoning effect can be avoided by use of the activated charcoal trap. Once poisoned, the mercuric oxide may be reactivated by passing pure air over the oxide at 250° C. and a flow rate of 200 to 300 ml. per minute. The process is completed in a few hours.

Effect of Moisture. Moisture does not interfere with the reaction of carbon monoxide with red mercuric oxide. Because of a strong tendency for water to be adsorbed by the oxide, however, even at 200° C., more reliable results are obtained if the gas sample is dried. Rigorous drying, such as is required by the iodine pentoxide and Hopcalite methods, is not necessary, and calcium chloride followed by magnesium perchlorate has been found ample, even when the gas is saturated with water vapor.

RESULTS

It is believed that the mercuric oxide method is capable of giving higher reproducibility and greater accuracy than any other method for the determination of carbon monoxide described in the literature. In addition to the analysis of many mixtures prepared in the authors' laboratories, this method was used in the analysis of three samples supplied by the National Bureau of Standards. Two of these unknowns were simultaneously submitted by the

Table III. Analyses of National Bureau of Standards Samples Submitted as Unknowns

	Unknown 1		Unknown 2		Unknown 3	
Detn. No.	Experimental *P.p.m.*	Deviation from mean *P.p.m.*	Experimental *P.p.m.*	Deviation from mean *P.p.m.*	Experimental *P.p.m.*	Deviation from mean *P.p.m.*
1	101.3	−0.1	111.3	0.7	395.1	−1.2
2	102.6	1.2	108.3	−2.3	393.8	−2.5
3	99.7	−1.7	111.2	0.6	396.3	0.0
4	98.9	−2.5	109.3	−1.3	398.4	2.1
5	103.1	1.7	110.5	−0.1	397.4	1.1
6	99.9	−1.5	111.5	0.9	394.3	−2.0
7	103.3	1.9	112.7	2.1	398.6	2.3
8	101.7	0.3	109.8	−0.8	396.8	0.5
9	100.4	−1.0	...	...	396.4	0.1
10	102.9	1.5	...	...	...	...
Av.	101.4	1.3	110.6	1.1	396.3	1.7
Reported value	101.0 ± 1.0		110.6 ± 0.9		396.3 ± 1.4	
True value[a]	99.99		108		393	

[a] Supplied by National Bureau of Standards after reports on analyses had been submitted.

Bureau of Standards to several key laboratories engaged in the investigation of the carbon monoxide problem. The true concentrations were not disclosed until after the analytical results were reported. An evaluation of the various methods and a comparison of the results from eight laboratories are given in a report of the National Bureau of Standards (*7*).

A copy of the results reported by the present authors is reproduced in Table III. This table is a complete report, including every determination made by use of the mercuric oxide method. At the time these results were reported, investigation of the air blank was still incomplete and correction was made only in the case of unknown 1. The correction of −0.4 p.p.m. which was applied was clearly too small and later work showed that it should have been about −1 p.p.m.

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Determination of Small Concentrations of Calcium and Magnesium

By Titration with Standard Soap Solution

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A previously described method has been modified to render it applicable to low concentrations of calcium and magnesium. The effect of alkalinity upon the determination is described and the conditions for a significant standardization are indicated. A practical application of the modified method is included, together with gravimetric results for the same samples.

A RAPID titration method for determining the hardness distribution in industrial waters, described by Polsky and Feddern (*3*), involves a direct titration for calcium with Clark's soap solution (*1*), after addition of ammonium chloride and a pH adjustment. The total hardness is then determined by the usual Clark method. The difference of the two gives magnesium hardness.

In attempting to apply this method to waters of low hardness, ranging from 5 to 50 parts per million of calcium carbonate, it was observed that the results did not agree with those obtained by conventional analytical procedures. An investigation was therefore undertaken to determine the reasons for the discrepancies.

It has for some time been observed that the amount of soap required by a given concentration of calcium or magnesium depends very markedly on the pH of the solution and for this reason it has become standard practice, in this laboratory, to perform all soap titrations at one pH—8.3, the first pink of phenolphthalein. The soap solution is also standardized at this pH. Unless this is done, it is impossible to obtain reliable results with soap on waters of low hardness.

In the light of this previous experience it was decided to make two standardizations of the soap solution, one at pH 8.3 and another at pH 11.7. The Polsky and Feddern method specifies pH 11.7. The standard Clark procedure is used with the exception of the neutralization to phenolphthalein in the first case.

The Polsky and Feddern method is as follows:

> To an 8-ounce shaking bottle are added 50 ml. of the sample, 1.0 ml. of 10% ammonium chloride, and 2.7 ml. of 1 *N* sodium hydroxide. Soap solution is then added in small increments until a foam forms which lasts 1 minute. The 1-minute foam was found unreliable and a 5-minute foam has been adopted in this laboratory. The lather factor, or blank, is included in the curve and concentrations are read directly from the curve. In Figure 1 the two curves obtained at two pH's are shown. The difference in soap required at the two pH's is readily seen.

From the curves and the assumption that total hardness minus calcium equals magnesium, it is apparent that if only one standard curve is used the magnesium will be high. If the curve at pH 8.3 is used the total hardness will be correct but the calcium will be too low. If the curve at pH 11.7 is used the calcium will be correct but the total hardness will be too high. This difficulty was encountered in attempting to apply the original method to waters of low hardness in this laboratory. A standard curve at each pH is clearly necessary.

In analyzing a water sample the total hardness is first obtained by proceeding as in the first standardization. The total hardness (expressed as p.p.m. of calcium carbonate) is read from the curve at pH 8.3. A second portion is then used for the calcium determination, which is carried out as in the second standardization. The calcium hardness is then read from the curve at pH 11.7. The difference of the two results is the magnesium hardness (expressed as p.p.m. of calcium carbonate).

Table I. Summary of Results on Standard Solutions

Total Hardness			Calcium Hardness			Magnesium Hardness		
Added	Determined	Difference	Added	Determined	Difference	Added	Determined	Difference
				Parts per million of calcium carbonate				
7.7	7.8	0.1	4.1	5.4	1.3	3.6	2.4	−1.2
11.3	11.4	0.1	4.1	5.3	1.2	7.2	6.1	−1.1
16.0	15.4	−0.6	12.4	12.4	0.0	3.6	3.0	−0.6
19.6	21.0	1.4	12.4	12.5	0.1	7.2	8.5	1.3
20.1	21.5	1.4	16.5	16.1	0.4	3.6	5.4	1.8
26.8	27.1	0.3	12.4	12.6	0.2	14.4	14.5	0.1
27.3	27.1	−0.2	16.5	17.0	0.5	10.8	10.1	−0.7
27.8	26.6	−1.2	20.6	20.4	−0.2	7.2	6.2	−1.0
31.4	30.9	−0.5	20.6	20.0	−0.6	10.8	10.9	0.1
35.0	33.0	−2.0	20.6	20.8	0.2	14.4	12.2	−2.2
35.5	33.1	−2.4	24.7	23.2	−1.5	10.8	9.9	−0.9
39.1	39.3	0.2	24.7	23.8	−0.9	14.4	15.5	1.1

After the standardizations were completed, various mixtures of calcium and magnesium standard solutions were titrated. In each case two titrations were made: one for total hardness, first adjusting the pH to 8.3, the other for calcium alone, with addition of ammonium chloride and sodium hydroxide. The neutralization to pH 8.3 must be accomplished very carefully to avoid precipitation of magnesium hydroxide which redissolves rather slowly.

The results obtained from the various mixtures are summarized in Table I.

The greater accuracy is obtained in the calcium determination. Since the magnesium soap is more soluble than the calcium soap, the calcium ion is first precipitated completely. Fahrion (*2*) has reported the solubility of magnesium oleate as 0.23 gram per liter and that of calcium oleate as 0.1 gram per liter. The magnesium ion, on the other hand, precipitates less rapidly, so that an evanescent end point is encountered. Therefore a permanent lather is here defined as 5 minutes. Very vigorous shaking will prevent mistaking the end point.

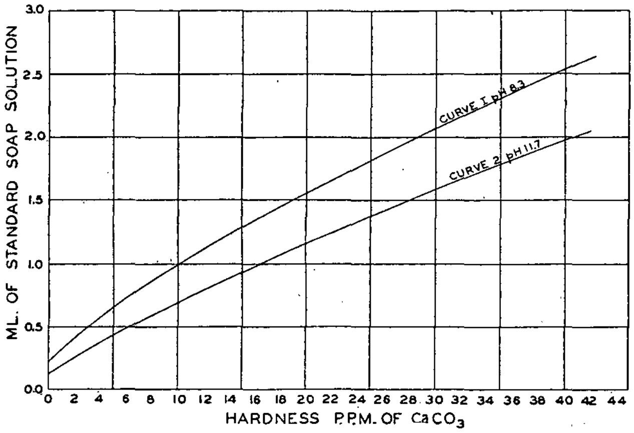

Figure 1

References to a "ghost point" have frequently been noted in textbooks and periodicals. At this point a semistable lather is said to be formed, when all the calcium has been precipitated. Presumably the semistable lather is the result of formation of a supersaturated solution of the magnesium soap, for further addition of soap is reported to destroy the lather. Use of this phenomenon has been advocated, from time to time, as a method of obtaining the hardness split. However, this is of little practical value, since it is not encountered in all types of water and, in fact, was never observed in this laboratory during the course of this work, although a great number of titrations were performed. An apparent end point may be observed at any point during the precipitation of the magnesium, if the soap solution is added in too large amounts, because of the slow rate of magnesium precipitation. The "ghost point" is, for this reason, regarded in this laboratory more as an incorrectly performed titration than as a useful indication of calcium hardness.

Practical Application of Method. Most high-pressure water-treating plants have a silica-removal unit that consists of a conical tank into which lime and magnesium oxide are fed. The two oxides form a flocculent suspension upon which silica is occluded. In operation, untreated water is fed into the bottom, the water passing up through the floc bed and then into an effluent pipe at the top. It is desirable to know just how much floc is carried up with the water, so that the level of the bed may be controlled in such a way that the carry-over is at a minimum.

To determine this, a sample is taken; part of it is filtered and another part is acidified. Filtering removes the floc; acidification dissolves it. The soap titrations are run upon these two samples, care being taken to make the pH adjustments first. In this way the dissolved calcium and magnesium are determined from the filtered sample and the dissolved plus the suspended calcium and magnesium are determined from the acidified sample. Thus, the amount of floc and its composition are found in this simple procedure. If it is also desired to find how much the hardness in the untreated water is increased in passing through a silica unit, the test may also be run on the untreated water; thus a complete check of the performance of the unit is made in a very short time.

The results of such a procedure are given in Table II together with results from gravimetric determinations.

From these data the information in Table III may be computed, to show the accuracy to be expected.

Although this modified method was developed for water samples with low concentrations of calcium and magnesium, it gives equally good results on hard water samples.

Table II. Water Treatment

	Magnesium		Calcium		Total Hardness	
	Soap	Gravimetric	Soap	Gravimetric	Soap	Gravimetric
			P.p.m. of calcium carbonate			
Untreated water	11.2	9.8	18.4	19.6	29.6	29.4
Filtered sample	3.5	3.6	41.3	42.0	44.8	45.6
Acidified sample	21.7	22.6	79.5	78.0	101.2	100.6

Table III. Comparison of Soap and Gravimetric Methods

	Soap	Gravimetric
Mg precipitated from untreated water	7.7/11.2 × 100 = 69%	6.2/9.5 × 100 = 65%
Ca increase in silica unit	41.3/18.4 × 100 = 224%	42.0/19.6 × 100 = 214%
Total hardness increase in silica unit	44.8/29.6 × 100 = 151%	45.6/29.4 × 100 = 155%
Mg in floc	(21.7–3.5)/(101.2–44.8) × 100 = 33%	(22.6–3.6)/(100.6–45.6) × 100 = 35%
Ca in floc	(79.5–41.3)/(101.2–44.8) × 100 = 68%	(78.0–42.6)/(100.6–45.6) × 100 = 65%
Floc carry-over	(101.2–44.8)/10,000 = 0.006%	(100.6–45.6)/10,000 = 0.006%

ACKNOWLEDGMENT

Sincere appreciation is expressed to M. H. Pramme and D. L. Sandretto of the Richmond Refinery and J. D. Hall of the Bakersfield Refinery for advice and encouragement generously extended during the course of this investigation.

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Hydroxylamine Method of Determining Penicillins

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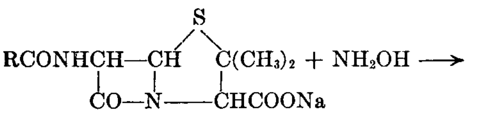
In a search for a rapid and precise method for assaying penicillins in fermentation liquors as well as finished salts, the hydroxylamine method of Staab, Ragan, and Binkley was modified to include the use of penicillinase-inactivated blanks to eliminate the effect of interfering substances. The method is based upon the fact that penicillin reacts rapidly with hydroxylamine to give a hydroxamic acid, which forms a purple complex with ferric ion, and this can be determined colorimetrically.

A RAPID and precise method for assaying penicillins in fermentation liquors as well as in finished salts was desired for determining yields in processing. The hydroxylamine method of Staab, Ragan, and Binkley (*13*) appeared the most promising of those described in the literature. It was found to give good results on finished salts that were 50 to 100% pure, but the values obtained on fermentation liquors were much higher than those indicated by the bioassay data. This difficulty was overcome by modifying the method to include the use of penicillinase-inactivated blanks. Since only a brief abstract of the original method has been published, the details are given in this paper.

The method is based upon the fact that penicillin (*3*) (I) reacts rapidly with hydroxylamine to give a hydroxamic acid (II) which forms a purple complex with ferric ion that can be determined colorimetrically (*13*). It is very similar to the method of Lipmann and Tuttle (*7*) for the determination of acyl phosphates. This reaction is not specific for penicillin, since many esters, anhydrides, and amides also react with hydroxylamine to produce hydroxamic acids. The hydroxylamine can also react with aldehydes or ketones to give oximes that form colored complexes with ferric ion (*12*). However, the effect of these interfering substances can be eliminated by the use of a blank which differs from the test solution only in the fact that the penicillin has been hydrolyzed to penicilloic acid (III) by means of the enzyme penicillinase (*4*). The action of this enzyme is believed to be specific for penicillin and the resulting penicilloic acid does not interfere.



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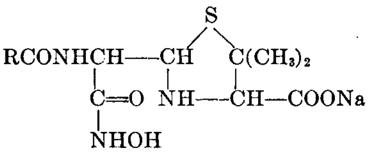

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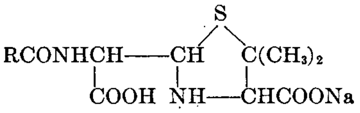

III

REAGENTS

Penicillinase Solution. The contents of a 100,000-unit vial of Schenley Penicillinase A were dissolved in 25 ml. of distilled water and placed in a dropping bottle. This solution was found to be stable for periods as long as 3 months when stored in a refrigerator.

Hydroxylamine Solution. A 4.0 *M* solution of hydroxylamine hydrochloride (70 grams of reagent grade hydroxylamine hydrochloride in 250 ml.) was mixed with an equal volume of 3.0 *M* sodium hydroxide. The resulting mixture (pH 6.4) has a limited stability and should not be used more than a few hours after it has been prepared. The hydroxylamine hydrochloride solution may be stored for several weeks at room temperature.

Phosphate Buffer. Sterile 2.5 millimolar pH 7 phosphate buffer was prepared by placing the solution in a bottle equipped with two-holed rubber stopper which held a siphon and an air-inlet tube attached to a glass tube packed with cotton. The entire apparatus was autoclaved for 15 minutes at 15 pounds per square inch (1.1 kg. per sq. cm.) steam pressure.

Acetate Buffer. One volume of 0.1 *M* acetic acid was mixed with 4 volumes of 0.1 *M* sodium acetate.

Ferric Chloride. A 10% solution of ferric chloride hexahydrate in 0.1 *N* hydrochloric acid was used.

PROCEDURE

Samples of solid penicillin salts were dissolved in sterile 2.5 millimolar phosphate buffer and diluted to a concentration about 0.25 to 2.0 millimolar. For benzylpenicillin (penicillin G) a 1.0 millimolar solution is equivalent to 594 Oxford units per ml. Fermentation liquors, if not previously clarified, were filtered through paper. To a 5-ml. portion of the test sample was added one drop of penicillinase solution and the mixture was allowed to stand at room temperature for 4 hours. It was found by Fred Hanson of these laboratories that incubation at 38° for one hour was equally effective.

Two milliliters each of the test solution and the acetate buffer were pipetted into a macrotube for the Evelyn photoelectric colorimeter. Two milliliters each of the penicillinase-inactivated test solution and acetate buffer were placed in a second colorimeter tube. (The colorimeter tubes should give identical readings with distilled water. The Evelyn "selected" tubes were found to be well matched but the Klett "calibrated" tubes varied as much as 10 scale divisions. From 90 of these "calibrated" tubes the author obtained a group of 12 that matched.) The interval timer was started and 2 ml. of the hydroxylamine solution were pipetted into each tube. When the timer read exactly 5 minutes, 2 ml. of the hydrochloric acid and then 2 ml. of the ferric chloride solution were pipetted into each tube. In all cases the reagents were added to the sample tubes first. When the timer read about 9.5 minutes the blank tube was placed in the instrument (540 filter) and the zero point adjustment was made. At exactly 10 minutes the reading on the sample was taken.

With the Klett-Summerson instrument (Klett 54 filter) the procedure was the same, except that 1-ml. volumes were used.

The above timing schedule makes it convenient to run test samples in groups of five. When this is done it is advisable to use volumetric pipets only for measurement of the sample and serological or "blow" pipets for measuring the reagents, as they deliver more rapidly.

STABILITY OF COLOR

The use of a strict timing schedule, especially for the interval between addition of the ferric chloride and reading the colorimeter, was made necessary by the unstable nature of the color. The change of color intensity with time, using a 1 millimolar penicillin solution, is shown in Table I.

Table I. Change of Color Intensity with Time

Time after Addition of Ferric Chloride, Minutes	Relative Intensity of Color
2	100
4	78
6	69
10	56

Several attempts were made to stabilize the color by decreasing the acidity. Citric acid held the iron in solution but changed the color completely. Oxalic acid, sulfuric acid, and the hydrochlorides of glycine, pyridine, and nicotinic acid gave satisfactory colors but did not improve the stability.

Table II. Effect of Phosphate Ion

Phosphate Concentration, Mole per Liter	Relative Intensity of Color
0.0	100
0.0025	99
0.25	58

Table III. Effects of Interfering Substances on Color Produced by 1.0 *mM.* Sodium Benzylpenicillin

	Relative Intensity of Color When Blanks Contained:	
Interfering Substance	Hydroxylamine, ferric chloride, and hydrochloric acid	Penicillinase-inactivated test solution
None	100	100
10% acetone (vol.)	111	85
Amyl acetate[a], saturated solution	108	101
Acetamide, 100 mg./ml.	438	98

[a] Technical grade (Pentasol, Sharples).

INTERFERING SUBSTANCES

Effect of Phosphates. Lipmann and Tuttle reported that in their acyl phosphate determinations the color intensity of the iron–hydroxamic acid complex was depressed by certain anions, including fluoride and phosphate and to a lesser extent oxalate and sulfate. In the present investigation the effect of phosphates has been studied. The others have been neglected, as it seemed unlikely that they would be present in amounts sufficient to cause trouble.

The pronounced effect of phosphate ion can be seen from the results given in Table II. A 1.0 millimolar solution of sodium benzylpenicillin was tested in the presence of pH 7 phosphate buffer.

In the present investigation 2.5 millimolar phosphate buffer was used to dissolve all solid penicillin salts. An average of ten determinations indicated that it caused a 1% depression in the color intensity, but this is probably within the experimental error.

Other Interfering Substances. Since the reaction with hydroxylamine to produce hydroxamic acids has been reported (*6*) to take place with amides, anhydrides, and esters, the effects of amyl acetate and acetamide as interfering substances were studied briefly. Furthermore, as oximes have been reported to give a color test with ferric chloride (*12*), acetone was also studied. A 1.0 millimolar solution of sodium benzylpenicillin was tested by two methods in the presence of the interfering substances. First, the comparisons were made using a blank containing only hydroxylamine, ferric chloride, and hydrochloric acid in order to determine the increase in color intensity caused by the reaction products of hydroxylamine and the interfering substances. In the second series the samples were read against penicillinase-inactivated test solutions which contained the interfering substances. The results are summarized in Table III.

In all cases the increase in color intensity caused by the interfering substances was corrected by using a penicillinase-inactivated portion of the test solution as the blank. The low result obtained in the presence of 10% acetone was probably due to the fact that the amount of hydroxylamine that reacted with the acetone was great enough to decrease substantially the amount available for reaction with the penicillin.

RESULTS OBTAINED

Pure Penicillins. The relationship between color intensity and concentration was studied on four different penicillins, using solutions that were prepared from analytically pure sodium salts. Using the Evelyn instrument, the color was found to be directly proportional to the concentration over the range of 0.4 to 4.0 millimolar (240 to 2400 Oxford units per ml. for penicillin G). With the Klett-Summerson instrument this range was from about 2 to 4 millimolar. The results obtained with benzylpenicillin (G) at 25° are given in Table IV (averages of 6 determinations).

Using the Evelyn colorimeter, penicillins F, K, and X were found to obey Beer's law over about the same concentration range but the colors produced were slightly less intense than with G. The relative intensities of color, measured in the range where Beer's law is applicable, are listed in Table V.

Table IV. Results with Benzylpenicillin

	Evelyn		Klett	
mM.	L[a]	L/mM.	G[b]	G/mM.
0.125	0.0268	0.214	..	..
0.375	0.0758	0.202	34	91
0.500	0.100	0.200	42	84
0.750	0.148	0.197	59	79
1.00	0.198	0.198	75	75
1.50	0.297	0.198	108	72
2.00	0.396	0.198	142	71
4.00	0.780	0.195	279	70
8.00	1.48	0.185	..	..

[a] L = 2-log of galvanometer reading.
[b] G = galvanometer reading (logarithmic scale).

While the differences in color intensity on a molar basis are rather large, they do not detract seriously from the usefulness of the method. For example, a mixture of 60% G, 15% F, and 25% K would give a molar intensity of 97 as compared with 100 for pure G. On a weight basis the differences, with the exception of penicillin K, are less pronounced.

The two aromatic penicillins G and X have higher molar intensities than do the aliphatic penicillins F and K. In only one (*5*) of the other published chemical methods (*1, 2, 5, 8, 9, 11*) has a direct comparison of results on the various penicillins been recorded.

Impure Mixed Penicillins. An accurate comparison between chemical and biological penicillin determinations is impossible because of the wide variation in biological potency (see Table V). However, a series of comparisons indicated that the methods agreed as well as could be expected (see Table VI). The bioassays were carried out in three control laboratories within The

Table V. Relative Color Intensities

Penicillin	G	X	F	K
R (see Formula I)	$C_6H_5CH_2$—	p-$HOC_6H_5CH_2$—	$CH_3CH_2CH{=}CHCH_2$—	n-C_7H_{15}—
Molecular weight of sodium salt	356	372	334	364
Relative color intensity, molar basis	100	99	93	92
Relative color intensity, weight basis	100	95	99	90
Biological activity, Oxford units per mg.	1667	900	1550	2300

Table VI. Impure Mixed Penicillins

		Bioassay		
Sample No.	Colorimetric Assay	Lab. 1	Lab. 2	Lab. 3
	A. Crude Calcium Salts			
K-4720	1080, 1080	1080	1240	1170
K-4721	1080, 1090	1200	1230	1130
K-4722	1200, 1220	1350	1330	1240
K-4723	1210, 1230	1290	1450	1590
K-4724	970, 1010	970	1180	1140
K-4725	1160	1020	1280	1380
26-AJF-2[a]	1640, 1620	1640	1780	...
31-AJF-2[a]	1650, 1640	1715	1560	...
	B. Fermentation Liquors			
K-4719	430, 460	480	420	...
K-4719S	320, 330	360	300	...
K-4720	470, 490	480	520	...
K-4721	380, 420	420	380	...
K-4722	530, 550	610	520	...
K-4723	470, 460	430	540	...
K-4725	450, 420	420	440	...

[a] Crystalline sodium salts.

Upjohn Company, using an adaptation of the hollow-cup agar-plate method *(10)*.

ACKNOWLEDGMENTS

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Determination of the Alcoholic Hydroxyl Group in Organic Compounds

Phthalic Anhydride Method

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Phthalization with phthalic anhydride in hot pyridine solution can be readily applied to the determination of alcohols or of the alcoholic hydroxyl content of complex mixtures of the type obtained in vapor-phase catalytic reactions involving alcohols. Aqueous alcoholic solutions can be analyzed. Aldehydes and other compounds found in such condensates do not interfere. Phenolic hydroxyl groups do not react. Amines react quantitatively or to excess. Polyhydroxy compounds with primary and secondary hydroxyl groups give satisfactory results; tertiary hydroxyl groups do not give satisfactory results. Volatile alcohols can be analyzed without difficulty.

IN THE course of a comprehensive investigation of methods for the quantitative determination of the hydroxyl group in organic compounds, the reaction of phthalic anhydride with various hydroxyl-containing compounds was studied, since it seemed to offer certain advantages over the acetic anhydride and other methods usually used for the estimation of this functional group. A simple method for the determination of the alcoholic hydroxyl group content of organic compounds, based on esterification with phthalic anhydride in pyridine solution, was developed and tested. It was found that the method can be used for the determination of the alcohol content of dilute aqueous solutions, and that such substances as ketones, saturated and unsaturated aldehydes, acids, esters, and phenols do not interfere. This method has been successfully applied to monohydric aliphatic alcohols from C_1 to C_8, various polyhydric compounds, and complex liquid condensates obtained from organic reactions.

The principal advantages of the method described in this paper are its specificity for alcoholic hydroxyl groups and its applicability to aqueous solutions. Its principal limitations are its inapplicability to tertiary hydroxyl compounds due to the dehydration of the latter, and the apparent excessive reaction of certain amines as discussed below.

The extensive literature up to 1937 on the determination of the hydroxyl group is reviewed by Meyer *(10)*.

The method most frequently used for the determination of hydroxyl groups, which was first proposed in 1901 by Verley and Bölsing *(23)*, is esterification by acetic anhydride in pyridine solution. More recent modifications by this method are described by Ogg, Porter, and Willits *(12)* and Christensen and his coworkers *(13)*. While this method has been successfully applied to the determination of most primary alcohols and many secondary alcohols, it is not readily applied to volatile compounds; aldehydes, especially those of relatively low molecular weight, interfere by reacting with the acetic anhydride; phenols react partially or completely, interfering with the direct determination of the alcoholic hydroxyl content of the sample; and the presence of more than a small amount of water in the sample renders the determination inexact or impossible *(26)*. The use of an acetyl chloride–pyridine complex suspended in toluene as the esterifying agent is described by Smith and Bryant *(21)*, who extensively investigated the applicability of the method to various types of hydroxyl-containing compounds. This method seems to offer some advantage over the use of acetic anhydride—e.g., the interference of aldehyde is less, although the presence of aldehydes has an unfavorable effect on the end point. Smith and Bryant give the average precision of the acetyl chloride method as ±0.2%; the absolute accuracy of the two methods is said to be comparable and, based on the data given, about 1% relative. Christensen, Pennington, and Dimick *(2)* obtained satisfactory results using acetyl chloride without a solvent.

Bryant, Mitchell, and Smith *(1)* have described a procedure based on the determination by the Karl Fischer method of the water produced on esterification of the hydroxyl group with acetic acid in the presence of boron trifluoride as catalyst. While the method can be applied to dilute aqueous solutions, phenols react incompletely, and carbonyl and some other types of compounds interfere by reacting with the reagent or the catalyst.

Other recently suggested methods for the determination of hydroxyl groups involve reaction with hydrogen iodide *(11)*, with acid chlorides of the higher fatty acids *(15)*, or with triphenylmethyl chloride *(17)*.

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The nature of the reaction of phthalic anhydride with various types of alcohols in benzene solution was investigated in 1899 by Stephan (*22*) and its use for determining primary alcoholic hydroxyl groups was suggested. Based on this work, Schimmel and Co. (*20*) developed and used a method for the approximate determination of primary alcohols such as geraniol and citronellol in essential oils. De Jong (*7*, *8*) examined critically this procedure for geraniol and found that the reaction was not quantitative but that compensating reactions may occur. The use of phthalic anhydride in benzene solutions has also been critically examined by others (*4*, *5*, *14*, *18*), who indicated that this procedure had no particular advantages to warrant its use and in many cases possessed definite disadvantages.

In 1926 Radcliffe and Chadderton (*14*) suggested the use of phthalization overnight at room temperature in pyridine solution for geraniol and other alcohols found in essential oils. These authors found that under the experimental conditions carboxyl compounds, esters, ethers, and phenols did not react at room temperature; primary amines apparently reacted quantitatively, secondary amines varied in the extent of their reaction, while tertiary amines and amides did not react. Analytical data for pure alcohols of the type found in essential oils were satisfactory; the results obtained for a number of industrial grade oils were, in many cases, different from those obtained by the acetylation method. Glichitch and Naves (*4*, *6*) found the method satisfactory for the estimation of essential oils. While this technique seemed more effective than phthalization in benzene, the required reaction time of 18 hours or longer as well as other disadvantages made improvement desirable. Sabetay and Naves (*16*, *19*) described phthalization in hot pyridine solution, which gave a more rapid and manageable method. These authors examined a comprehensive group of compounds, although in most cases only a single determination on each compound was reported. They found the method to be applicable to primary alcohols (93% to 96% of the calculated hydroxyl content being found) and to certain secondary alcohols; glycerol and 1,2-propylene glycol, among others, gave poor results. Glycerol, calculated as possessing three hydroxyl groups, gave 63% of the calculated hydroxyl content, which is equivalent to 96% of the expected hydroxyl content if only the two primary hydroxyl groups are assumed to react.

Unfortunately, the phthalization procedure involving reaction in hot pyridine solution, which seemed to the present authors the most suitable method for their purposes, has been applied almost entirely to the determination of the hydroxyl-containing compounds which occur in essential oils. It has not been sufficiently investigated as regards its applicability to the determination with an accuracy of one part in a hundred of ethanol and other lower alcohols as well as glycols and other compounds containing secondary hydroxyl groups. No study has been made of the interference which may be expected from water and organic compounds such as aldehydes which might be present in typical liquid products resulting from the reaction of ethanol or other alcohols—e.g., no results are given by previous workers for the analysis of mixtures of compounds. The purpose of this paper was to develop a technique which would answer the points mentioned and which would, it was hoped, call to general attention the applicability of phthalization in pyridine solution for analyzing complex organic mixtures.

REAGENTS AND APPARATUS

The reagents used in the studies described were Mallinckrodt's analytical reagent grade phthalic anhydride, Barrett's refined grade 2A pyridine, 0.35 *N* standard sodium hydroxide solution, and a 1% alcoholic solution of phenolphthalein indicator. The hydroxyl-containing compounds analyzed were distilled in most cases and a narrow-boiling fraction was used; the probable purity is indicated in Table I.

Barrett's grade 2A pyridine as obtained commercially contains a significant amount of water and other substances which interfere with the accuracy of the determination. In order to eliminate these substances, the pyridine should be distilled from over barium oxide and only the portion distilling at 115° C. used. The phthalization mixture is prepared by dissolving 20 grams of phthalic anhydride in 200 ml. of purified pyridine; this solution is prepared fresh daily.

The apparatus required depends partly on the procedure selected. It was found satisfactory to carry out the reaction either under reflux or by the use of pressure bottles. Inasmuch as the pressure bottle technique is somewhat simpler and more rapid, this is described in detail below. For this technique, citrate of magnesia bottles of 1-pint capacity are used. An air bath set at 100° ± 2° C. is required; an ordinary laboratory drying oven will suffice.

It is preferable that the pyridine used be anhydrous and the reaction equipment, whether pressure bottles or flasks and condensers, be thoroughly dried. Unless these precautions are observed low values may be obtained; water hydrolyzes the phthalic anhydride and may thereby reduce the concentration below the excess required.

Table I. Analysis of Hydroxyl Compounds by the Phthalization Method

Compound	Purity as Determined by Physical Constants	Purity by Phthalization Method	Recovery by Phthalization Method
	Wt. %	*Wt. %*	*%*
Methanol	99.3	100.0, 100.2	100.8
Ethanol	100.0	100.7, 100.7 100.3, 100.4	100.5
1-Propanol	98.4	98.1, 97.9	99.5
2-Propanol	99.6	97.6, 97.6	98.0
1-Butanol	100.0	100.6, 100.6	100.6
2-Methyl-1-propanol (isobutyl alcohol)	...	101.8, 101.2	...
Cyclohexanol	95–96	95.1, 95.1	99–100
2-Ethylhexan-1-ol	99	99.1, 99.1	100
2-Octanol	97–98	96.0, 96.3	98–99
Ethylene glycol	99	98.7, 98.7	99.5
Propylene glycol	100	99.4, 99.6	99.5
Glycerol	95.5	87.9, 87.9 94.9[a], 94.3[a]	92.0 99.1
Benzyl alcohol	100	99.4, 99.7	99.6

[a] Two hours at 100° C. allowed for reaction.

ANALYTICAL PROCEDURE

For samples containing a high percentage of ethanol, a sample weighing 1.0 to 1.5 grams is carefully pipetted into a 50-ml. volumetric flask containing 30 to 40 ml. of the purified anhydrous pyridine which has been weighed, care being taken to avoid wetting the neck of the flask; for monohydric alcohols of higher molecular weight and dilute solutions of ethanol, samples of correspondingly larger weight should be taken. After reweighing, the solution is made up to volume with pyridine and mixed thoroughly by shaking.

In certain cases where the sample is extremely volatile—i.e., contains considerable material boiling below 40° C.—the sample is weighed directly in thin-walled glass ampoules. The ampoule is then transferred to the volumetric flask containing pyridine and is crushed under the surface of the pyridine by a glass rod. The rod is rinsed with pyridine on withdrawal, the solution is made up to volume with pyridine, and the contents of the flask are mixed.

Into a clean, dry, pressure bottle are pipetted 25 ml. of the phthalic anhydride solution by means of an automatic Machlett pipet or buret or a Lowy pipet. To this are added 10 ml. of the solution containing the sample. The sealed bottle containing the mixture is placed in an air oven set at 100° C. and is heated at that temperature for one hour. At the end of this time, the pressure is carefully released and 50 ml. of distilled water are added. After mixing, the solution is cooled under the cold water tap and titrated immediately with standard 0.35 *N* sodium hydroxide, phenolphthalein being used as an indicator.

A blank determination is made in the same manner on the reagents employed.

The difference in amount of alkali consumed between the sample and the blank represents the amount of esterifiable hydroxyl present in the solution:

$$\% \text{ hydroxyl} = \frac{V \times N \times 1.70}{W}$$

where W = weight in grams of the sample in the aliquot taken; V = volume in milliliters of standard sodium hydroxide solution used by sample, which equals the difference in volumes required by the blank and sample titrations; and N = normality of the standard sodium hydroxide solution.

DISCUSSION OF PROCEDURE

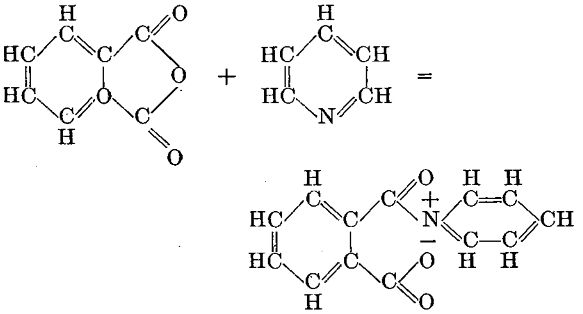
Size of Sample. The weight of sample taken should be such as to have present a minimum of 100% molar excess of phthalic anhydride over the amount required. The presence of a sufficient excess of anhydride can be noted by the formation of a yellow color in the solution after heating for the prescribed length of time. Unless this color appears the results may not be reliable. Failure of the color to appear indicates an insufficient excess of the reagent due to too large a sample or the presence of too much water.

Acidic Samples. Separate portions of samples containing free acid or acidic groups on the hydroxyl-containing compounds should be titrated with the standard alkaline solution at room temperature, using phenolphthalein as indicator, and a suitable correction made in the volume of alkaline solution consumed in the phthalization procedure.

Contact Time. While an hour is specified for the phthalization reaction, in many cases this time can be reduced to 30 minutes or less. In dealing with mixtures containing substances which react with phthalic anhydride on prolonged heating, it would be worth while to determine the minimum reaction period necessary for the hydroxyl-containing compounds involved. The reaction mixture, after the addition of the water, should be cooled and titrated in a minimum amount of time to avoid the possibility of the phthalate esters formed hydrolyzing to any appreciable extent; ordinarily, the danger of such reaction is almost nil. There was no measurable consumption of phthalic anhydride due to polymerization, decomposition, or other reactions in blank samples heated up to 4 hours.

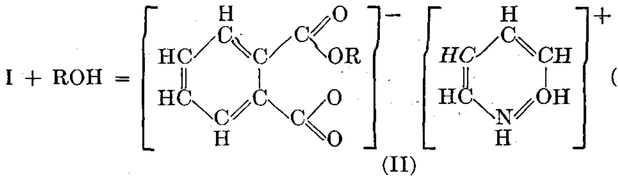
End Point. Although the pink phenolphthalein end point is normally easily detected, it is masked to some extent in this determination by the yellow color of the final solution. Therefore, instead of a color change from colorless to pink, there is a gradual transition from yellow to brown to orange to pink. It is felt that a representation of the true end point is the first noticeable permanent color change of the solution—without having to continue the titration until the color is definitely pink. After several titrations this point can be detected without any difficulty. The use of the mixed indicator, thymol blue-cresol red, offered no appreciable advantage over the use of phenolphthalein. In the case of dark-colored solutions the end point can be determined electrometrically. In a comparative series of runs on ethanol, the three methods of determining the end point gave the following per cent recoveries: phenolphthalein: 99.2, 99.3, 99.3, 99.3, 99.3; thymol blue-cresol red: 99.0, 98.8; electrometric (Beckman Model G pH meter): 98.7, 99.3, 99.3, 98.6.

Nature of the Reaction. Although the authors have not determined the nature of the intermediates formed during the reaction, it seems probable that the reaction proceeds in an analogous fashion to that postulated for acetylation in pyridine solution by Smith and Bryant (*21*). The phthalic anhydride reacts with the pyridine to form an addition compound which reacts with the hydroxyl-containing compound as shown:



(1)

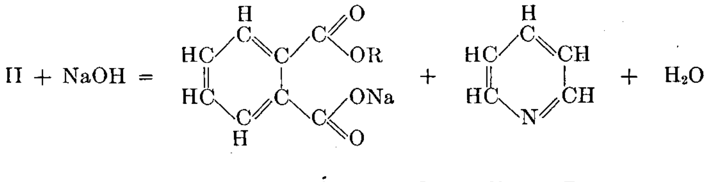
(I)



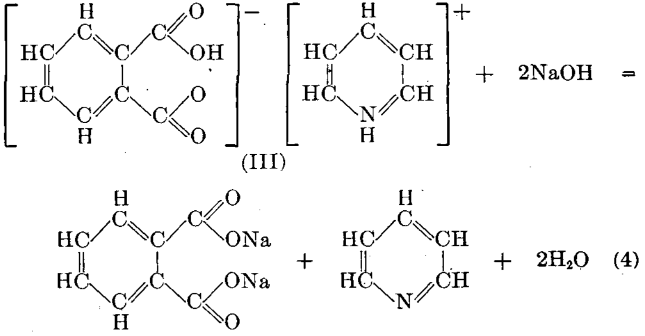
(2)

(II)

On addition of water the excess of compound I is hydrolyzed, forming a compound (III) analogous to compound II where the organic residue, R, is replaced by a hydrogen ion. Titration with alkaline solution converts compound III as well as compound II to the sodium salts and pyridine:



(3)



(III)

(4)

From these equations it can be seen that each equivalent of hydroxyl group present decreases by one equivalent the amount of alkaline solution required to neutralize the phthalization solution.

DATA AND DISCUSSION

Known Mixtures. A sample of Publicker absolute ethanol, which was found to contain 99.5% ethanol on the basis of its specific gravity and refractive index, was used throughout all the preliminary experiments. The water content of this sample was 0.44% by the Karl Fischer procedure.

Various modifications of the procedure recommended by Sabetay and Naves (*16*, *19*) were tried with varying degrees of success. The method described, employing pressure bottles, was found the simplest and gave satisfactory results. Good accuracy and precison were also obtained by refluxing the reaction mixture for one hour in a boiling water bath.

In Table I are given the results obtained by the phthalization method on various monohydric and polyhydric organic compounds. Low results were obtained when glycerol was permitted to react for 1 hour; a 2-hour period of heating gave a recovery of 99.1%. Phenol, *o*-cresol, and 1-naphthol showed a zero esterifiable hydroxyl content, indicating the specificity of the phthalization procedure for alcoholic hydroxyl under the conditions used; excellent results were obtained with benzyl alcohol. Acetaldehyde dibutyl acetal showed a hydroxyl content of about 9% based on that available by complete decomposition of the acetal, indicating some dissociation of the acetal during the phthalization procedure. While diethylamine showed a satisfactory reaction by the phthalization procedure, 100.1% recovery being obtained, 107 and 112% recoveries were found for small samples of aniline, and 134 and 135% for large samples; 103 and 109% recoveries were found in the attempted determination of ethylenediamine (1,2-diaminoethane). The abnormal results obtained with some amines may be due to phthalimide formation.

However, the phthalization procedure can apparently be applied to the quantitative determination of at least certain amines (cf. also *4*, *14*).

In Table II are given the results of analyzing one monohydroxyl and four polyhydroxyl compounds, which gave poor results. The purity of the samples of 2-methyl-2-butanol and of the 2-methyl-2,4-pentanediol exceeded 95%; the other three compounds were used without purification and were believed to be not less than 85% pure. Results for any given compound in Table II on the same horizontal line were obtained at the same time—i.e., on the same batch of samples. The results for 2,3-butanediol are probably correct in view of the consistent values obtained for samples heated for 1 hour and for 4 hours, while the 1,3-butanediol apparently required 2 hours of reaction for complete esterification. The results for the 2-methyl-1,2-propanediol are probably meaningless, as in the presence of even dilute acids the compound dehydrates and rearranges readily to give isobutyraldehyde (*25*). The unsatisfactory results for 2-methyl-2-butanol and 2-methyl-2,4-pentanediol are due to the ease with which tertiary alcohols are dehydrated in the presence of acidic catalysts (*24*). Investigation of the literature showed that 2-methyl-2,4-pentanediol can be dehydrated in the liquid phase in the presence of acidic catalysts to 2-methyl pentenols and 2-methyl pentadienes (*3*, *9*). The results obtained using stoichiometric molar ratios of 1-2, 1-1, and 2-1 of phthalic anhydride and 2-methyl-2,4-pentanediol in pyridine solution plus the data in Table II indicate that phthalic anhydride apparently causes the conversion of the methyl pentanediol to the methyl pentenol. The results obtained for 2-methyl-1,2-propanediol, which is also a tertiary alcohol, may be explicable in part on the basis of the same reaction; only about half of the expected hydroxyl content is available for esterification. Furthermore, 2-methyl-2-butanol, which is very readily dehydrated (*24*), shows very little esterification. It is hoped to investigate further the reaction of polyhydroxyl compounds with phthalic anhydride.

Table II. Analysis of Hydroxyl Compounds by Phthalization Method

Compound	Apparent Purity, Weight Per Cent for Different Reaction Times at 100° C. 1 hour	2 hours	4 hours
1,3-Butanediol	84, 84	96, 89	
	79, 78	92, 91	93, 92
	75, 76		
2,3-Butanediol	89, 89	91, 90	89, 90
	89, 89		
2-Methyl-1,2-propanediol (isobutylene glycol)	54, 54	59, 59	
	53, 53	59, 60	64, 64
	54, 53		
2-Methyl-2-butanol (*tert*-amyl alcohol)	3, 3	5, 5	10, 11
2-Methyl-2,4-pentanediol (preparation I)	45, 46		
2-Methyl-2,4-pentanediol (preparation II)	43, 42	52, 51	56, 58
2-Methyl-2,4-pentanediol (preparation III)	51, 50	50, 57	60, 60

In order to determine whether other substances possibly present in the liquid condensates obtained in catalytic organic reactions would affect the accuracy of the hydroxyl determination, synthetic mixtures were prepared containing known amounts of water and of representative members of various types of organic functional groups, including carbonyl compounds, acids, esters, and unsaturated compounds. Ethanol was determined in the presence of these substances singly and in mixtures; results of this study, shown in Table III, indicate that such substances, present in amounts likely to be encountered in reaction mixtures, do not interfere with the determination of the esterifiable hydroxyl group. Of particular interest is the accuracy attainable in mixtures containing as much as 85% of water.

Table III. Analyses of Synthetic Mixtures Containing Ethanol

	Constituents of Mixture	Composition *Wt. %*	Ethanol Found %
1.	Ethanol	79.4	79.6, 79.7, 79.7
	Water	20.6	
2.	Ethanol	14.6	14.5, 14.7
	Water	85.4	
3.	Ethanol	75.2	75.3, 74.8, 75.0, 75.0
	Water	19.6	
	Acetaldehyde	5.2	
4.	Ethanol	71.7	71.3, 71.1, 71.4
	2,4-Hexadiene	4.7	
	Water	18.7	
	Acetaldehyde	4.9	
5.	Ethanol	11.3	11.4, 11.3
	Acetic acid	27.2	
	Acetone	13.5	
	Crotonaldehyde	24.0	
	Ethyl acetate	17.6	
	Phenol	6.3	

Table IV. Alcohol Content of Condensate and Condensate Fractions

Fraction Boiling Range ° C.	Fraction of Total Condensate *Wt. %*	Ethanol by Phthalization *Wt. %*	Ethanol on Basis of Total Condensate *Wt. %*
<10	0.8	....	...
10–25	1.1	0.0	0.0
25–40	0.8	0.88, 0.91	0.01
40–75	2.9	32.27, 32.02	0.93
75–80	59.5	92.30, 92.37	54.94
80–90	2.2	64.35, 64.01	1.41
90–100	13.7	8.99, 8.60	1.20
Residue and holdup	19.0		
Total	100.0		58.5
Original condensate		59.0	

The data reported in Tables I and III indicate that the esterifiable hydroxyl content of the organic compounds analyzed with the exceptions noted could be determined with an average precision of 3 parts per thousand and an accuracy of approximately 1% relative.

Complex Samples. To determine the applicability of the phthalization procedure to the analysis of a very complex mixture, a sample of the liquid condensate obtained by cooling to 0° C. the effluent of the one-step vapor-phase catalytic process for the conversion of ethanol to 1,3-butadiene was analyzed. This sample contained butadiene, butenes, pentenes, hexenes and hexadienes, ethanol, *n*-butanol, acetaldehyde, diethyl ether, water, and other substances such as C_6 alcohols, high-boiling oils, etc. The results obtained on the original condensate were compared with those obtained when the condensate was fractionally distilled at high reflux ratio through a Stedman column containing 2 feet of packing and the individual fractions were analyzed by the phthalization procedure. Table IV contains the data obtained in this study. Similar results were obtained on analyzing another condensate sample, using the reflux technique.

Any material present in the sample capable of reacting with phthalic anhydride will cause erroneous results. Specifically, butanol, present in the higher boiling fraction of the condensate, reacted with the phthalic anhydride and caused the results for ethanol to be high. Since the molecular weight of butanol is 1.6 that of ethanol, the per cent error due to this substance, when reported as ethanol, will be equal to 0.6 of the percentage of butanol actually present. On this basis, the figure given for ethanol in the 90° to 100° C. fraction (Table IV) should be deducted from the total figure; the former figure, 1.2%, corresponds to 1.9% butanol. The ethanol content reported for the 80° to 90° C. fraction may also be partially due to butanol. However, since the sum of the ethanol and butanol was the same in both the original condensate and the total of the fractions analyzed, the results regarding the amounts of esterifiable hydroxyl group present calculated as ethanol are valid.

The ethanol content of the 75° to 80° C. alcohol fraction of another condensate was determined by phthalization to be 93.0%. This alcohol fraction contained, in addition to ethanol and water, hexadiene and minor amounts of other compounds. To this fraction was added absolute ethanol, so that the final concentration was 96.1% on the basis of the 93.0% figure. The ethanol content of this mixture obtained by the phthalization method was 95.8%.

SUMMARY

The determination of the alcoholic hydroxyl group by esterification with phthalic anhydride was investigated. By modifying the procedure suggested by Sabetay and Naves (*17*, *18*) and standardizing the conditions used, satisfactory results were obtained for a variety of compounds containing alcoholic hydroxyl groups. Phenolic hydroxyl groups do not react with the reagent. Amines react completely or to excess.

Using absolute ethanol a precision of 1 to 2 parts per thousand and an accuracy of 4 to 6 parts per thousand were achieved. In general, a precision of 2 to 3 parts per thousand and an accuracy of one relative per cent are obtainable.

Work with synthetic mixtures and a complex condensate from a vapor-phase catalytic reaction showed that the presence of water and several types of organic compounds, including aldehydes, does not interfere with the determination of the alcoholic hydroxyl content.

ACKNOWLEDGMENT

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Rapid Determination of Moisture in Liquid Sulfur Dioxide

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The current phosphorus pentoxide method for analysis of moisture in liquid sulfur dioxide is time-consuming and involved. A new method, using Karl Fischer reagent and employing a specially developed system to prevent contamination of the sample by moisture, is superior to the phosphorus pentoxide technique for control purposes. This article describes the equipment and technique employed in determining the moisture content of liquid sulfur dioxide by the Karl Fischer method and compares the results obtained by both methods. Emphasis is laid on the necessary precautions, description and use of equipment, method of analytical procedure, and comparative data between the conventional and new methods. Data show the accuracy and reproducibility of the Karl Fischer method.

LIQUID sulfur dioxide has assumed great importance in the industrial world. It is used extensively as a refrigerant, bleaching agent, preservative, and fumigant, in tanning processes, and in the manufacture of other chemicals.

The moisture content of liquid sulfur dioxide must be accurately determined, since its presence, even in very minute quantities, is highly detrimental to metallic equipment. A common analytical procedure called the phosphorus pentoxide method involves the weighing of water absorbed on phosphorus pentoxide.

Two Midvale tubes, each containing a thin layer of asbestos wool on the bottom, are placed in train form and charged with fresh phosphorus pentoxide. The tubes are then seasoned, or saturated with dry sulfur dioxide gas, for about 2 hours. A tare weight of the tubes is obtained. A known amount of liquid sulfur dioxide is evaporated through the phosphorus pentoxide tubes, which are connected in series where water is absorbed and weighed. One of the tubes is used as a counterpoise in weighing to correct for changes in atmospheric conditions during the test. This method takes several hours to run and involves a special technique for charging the Midvale tubes and connecting them in a rather complicated system employing an air-aspirator, mercury manometer, by-pass valves, special sample cylinder, and sulfuric acid and bubbling tubes, all of which must be maintained and checked periodically.

For control purposes, this method is difficult and time-consuming, and in order to keep abreast of production and obtain more accurate results, the Karl Fischer method (*1*) was successfully employed. However, because of the high hygroscopicity of liquid sulfur dioxide, very erratic results were obtained if the proper precautions were not taken. Moisture absorption in the sample

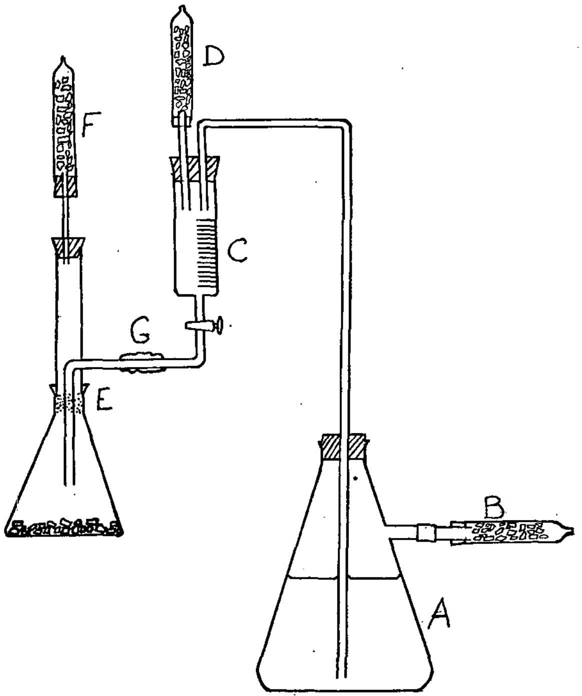

Figure 1. Sampling and Titrating Apparatus

and titrating system was successfully prevented by the use of the technique and apparatus described below.

APPARATUS AND REAGENTS

A 50-ml. calibrated dropping funnel with a center section having a 24/40 ground-glass joint is used to measure the volume of sample. Three tubes containing indicating grade activated alumina protect the titrating system from access of moisture from the air. A 500-ml. suction flask serves as the sample container. Three 300-ml. Erlenmeyer flasks containing Drierite and, lastly, a Karl Fischer buret which is also provided with tubes of indicating grade activated alumina are also employed. The reagents used are Karl Fischer reagent (standardized, *2*) and absolute methyl alcohol (standardized, *3*).

SAMPLING TECHNIQUE

Clean and thoroughly dry a 500-ml. suction flask, *A*, by rinsing with absolute methyl alcohol and drying in an oven at 110° C. After cooling in a desiccator, connect the flask to a line running from the sulfur dioxide cylinder, and draw off approximately 200 ml. of sample. Remove the line from the flask, attach a tube of indicating grade activated alumina, *B*, to the side arm, and temporarily stopper the flask. Fit a two-hole rubber stopper into the mouth of a 50-ml. graduated dropping funnel, *C*. To one hole, attach a drying tube containing activated alumina, *D;* to the other hole, connect a U-tube to lead to a one-hole rubber stopper fitted in the mouth of the sampling bottle. Allow one arm of the tube to extend to 0.6 cm. (0.25 inch) from the bottom of the sampling bottle. Place a 300-ml. Erlenmeyer flask containing 25 grams of Drierite on the ground-glass dropping-funnel joint, *E*. Attach a drying tube, *F*, containing Drierite on the neck of the dropping funnel. Wrap a piece of cloth, *G*, around the side arm of the dropping funnel to retain atmospheric moisture that might condense there and thereby introduce water into the titrating flask.

ANALYTICAL PROCEDURE

Place the thumb over the end of drying tube *B* on the side arm of the sampling bottle. The pressure of the sulfur dioxide forces liquid sulfur dioxide up into the measuring tube and into the dropping funnel. When 50 ml. have collected, release pressure and immediately drain the sample from the dropping funnel into the 300-ml. Erlenmeyer flask containing 25 grams of Drierite. This will flush out the system. Replace the 300-ml. Erlenmeyer with a dry Erlenmeyer flask containing 25 ml. of standardized methanol. Run up exactly 30 ml. of sample into the dropping funnel and drain into the flask. Remove the flask and replace it immediately with a flask containing Drierite. Titrate the solution of sulfur dioxide and methanol with Karl Fischer reagent in a Karl Fischer buret in the usual manner.

Sample Calculation.

E = ml. of Karl Fischer reagent for sample
F = ml. of Karl Fischer reagent for alcohol blanks
D = water equivalent of reagent as grams of water per ml.
G = specific gravity of sulfur dioxide at its boiling point (1.460)

$$\frac{(E - F) \times D}{\text{ml. of sample} \times G} \times 10^6 = \text{p.p.m. of moisture}$$

ACCURACY

In order to determine the accuracy of this technique, known amounts of water were added to samples of sulfur dioxide whose moisture content had been previously determined by the Karl Fischer method. A known amount of water was weighed from a Lunge pipet into 25 ml. of standardized absolute alcohol, and the liquid sulfur dioxide sample was then added as described above and titrated. Results are given in Table I.

A comparison was made on four samples, and a general agreement of both methods was obtained (Table II).

Table I. Accuracy of Technique

H_2O Added *P.p.m.*	H_2O Found by Karl Fischer[a] *P.p.m.*
500	495
1000	1000
1500	1497

[a] Total Karl Fischer value minus blank for water already present.

Table II. Comparison of Karl Fischer and Phosphorus Pentoxide Values

Water Found, P.P.M.	
Karl Fischer values	P_2O_5 values
78 (check 82)	82
40 (check 40)	45
26 (check 27)	24
20 (check 21)	31 (check 20)

Table III. Reproducibility of Method

Water Found, P.P.M.	
Sample 1	Sample 2
949	203
949 (check)	203 (check)
952 (check)	203 (check)
952 (check)	207 (check)
952 (check)	203 (check)
952 (check)	203 (check)

REPRODUCIBILITY OF METHOD

Six determinations for water content were made on two samples taken from different cylinders of liquid sulfur dioxide. The reproducibility obtained is directly related to the analyst and equipment used.

ACKNOWLEDGMENT

Acknowledgment is made to W. S. Seaman and H. J. Rodenberger for suggestion of this problem, and to A. G. Hill and associates for helping to prepare this paper.

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Anthrone in Estimating Low Concentrations of Sucrose

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A procedure is presented for the estimation of sucrose concentrations in the range of 10 to 250 parts per million, using a 0.05% solution of anthrone in concentrated sulfuric acid. This method offers the advantages of increased sensitivity and accuracy over the commonly used Molisch α-naphthol test.

ONE of the most common tests in sugar processing factories is the estimation of the sucrose content of various condensed vapors and solutions in which the sucrose content lies in the range of 10 to 250 p.p.m., where it cannot be accurately measured by polarimetric means. In such cases, the sucrose content is universally estimated by the Molisch α-naphthol test. Since this is a ring test, it cannot be adapted readily to transmittancy measurements and the sucrose content of a solution is usually reported after visual estimation to be a trace, light, or heavy.

The use of anthrone dissolved in concentrated sulfuric acid was suggested by Dreywood (*1*) as the reagent in a qualitative test for carbohydrates. The extreme sensitivity of this test, plus the fact that it is not a ring test, made it appear to be a promising improvement. The anthrone reagent has been used by the author to develop a procedure for the quantitative determination of sucrose in low concentrations.

PROCEDURE

The solution to be tested (2.0 ml.) is measured into a clean, dry 15 × 125 mm. Pyrex test tube and 3.0 ml. of 0.05% anthrone dissolved in concentrated sulfuric acid (reagent grade) are added so as to form a bottom layer. The tube is then shaken to effect complete mixing. The transmittancy of the solution for white light is next measured in a photoelectric colorimeter. Distilled water is used as the standard, with its transmittancy taken to be 1.000. By reference to a previously prepared calibration curve or table, the concentration of sucrose in the original sample is ascertained. Table I and Figure 1 present calibration data obtained with a Lumetron photoelectric colorimeter, Model 402E, manufactured by the Photovolt Corporation, New York, N. Y.

The sample and the reagent are shaken together as one shakes down the mercury in a clinical thermometer, with care being taken to prevent spilling. If for reasons of safety it is not desired that the tube be shaken, a small glass stirrer may be used. Inasmuch as the color-forming reaction is highly sensitive to temperature, it is important that the test be performed in a standardized manner. Variations in procedure will change the temperature rise caused by the heat of dilution of the acid and hence change the amount of blue-green coloring matter produced by a given sucrose concentration.

METHOD OF COLOR MEASUREMENT

The photoelectric colorimeter provides the most accurate and convenient method of color measurement. Various types of instruments can be used, depending on the degree of precision required. For the average factory laboratory, a single photocell colorimeter in which the transmittancy is indicated by the deflection of a microammeter is probably suitable. This may be calibrated using the particular test tubes (usually 15- to 18-mm.) which fit the holder. The data presented in Table I were taken from two runs made on successive days with sucrose solutions which were freshly prepared just before the tests were conducted. It is difficult to evaluate the precision of the method with only two runs, but the difference between these runs amounts to about 2%, based on the sucrose content.

Table I. Light Transmittancy of Sucrose Solution-Anthrone Mixtures

Solutions	Transmittancy	
Distilled water	1.000[a]	1.000[b]
Anthrone reagent + distilled water	0.791	0.783
Anthrone reagent + 10 p.p.m. sucrose solution	0.659	0.658
Anthrone reagent + 25 p.p.m. sucrose solution	0.493	0.498
Anthrone reagent + 50 p.p.m. sucrose solution	0.317	0.323
Anthrone reagent + 125 p.p.m. sucrose solution	0.115	0.109
Anthrone reagent + 250 p.p.m. sucrose solution	0.024	0.024

[a] Anthrone reagent prepared 4 hours previously.
[b] Anthrone reagent prepared 27 hours previously.

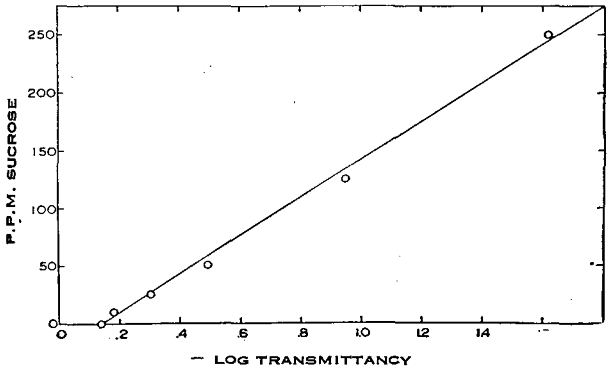

Figure 1. Light Transmittancy of Sucrose Solution-Anthrone Mixtures

If it is desired to use a visual comparison method, Lovibond standard color plates may be used in a suitably constructed comparator. It is possible to make close matches between the plates and the coloring matter produced in the anthrone test. This method offers an advantage if the samples are turbid because one can disregard the turbidity to a large extent in matching colors.

Primary standards made up from the anthrone reagent and sucrose solutions of known concentration and sealed in Pyrex tubes were not found to be satisfactory because the blue color gradually fades and the solutions become slightly cloudy. At the higher sugar concentrations, a slight amount of dark-colored material coats the inside of the tubes.

EFFECT OF IMPURITIES

The impurities commonly present in the condensed water samples of a beet sugar factory do not interfere seriously in this test. Solutions of diffusion juice, thick juice, molasses, and Steffen filtrate were prepared, each containing 200 p.p.m. of sucrose. The blue-green colors formed in the first three solutions were closely the same, but an olive-green color was obtained with the Steffen filtrate sample. This is not surprising when the low sugar-to-solids ratio of this material is considered. A special calibration would be required for the accurate measurement of the sucrose content of condensed waters containing Steffen filtrate.

REAGENT STRENGTH AND KEEPING PROPERTY

Dreywood (*1*) recommended that the strength of the reagent be 0.2%. Preliminary experiments showed that the reagent strength could be reduced to 0.05% and still give tests of sufficient sensitivity to permit distinguishing between solutions containing

10 and 25 p.p.m. of sucrose. The more dilute reagent offers an advantage because its bright yellow color is reduced. By using tubes of greater diameter, the strength of the reagent may be still further reduced. This offers no particular gain because an increased volume of reagent is required and, furthermore, the large test tubes are inconvenient to handle in making many routine measurements.

The anthrone used in this work was prepared according to the method in "Organic Syntheses" (*2*). Solutions of this material in concentrated sulfuric acid turned a brown-green color overnight. Since the presence of an impurity was suspected, the anthrone was recrystallized from glacial acetic acid to yield material which slowly changed to an orange-green color on long standing. A second recrystallization from the same solvent was of benefit, but not a third. Possibly one recrystallization would be sufficient if an excess of solvent were used and the anthrone slowly crystallized and well washed with fresh solvent.

In order to test the keeping property of the anthrone reagent, various samples of anthrone in concentrated sulfuric acid were sealed in 18-mm. (outside diameter) Pyrex tubes and stored at room temperature. One sample was stored at 0° to 1° C. The transmittancies of the tubes relative to distilled water were measured at intervals. In Figure 2 they are plotted relative to the initial transmittancy. These measurements were made in a Photovolt Lumetron colorimeter using unfiltered light.

The apparent anomaly that material which was recrystallized three times developed color faster than material which was recrystallized twice is believed to be due to the fact that the room temperature was higher during the test period on the former material.

Even solutions prepared from the purified anthrone and reagent grade sulfuric acid slowly darkened to an orange color on standing. Fresh solutions or older solutions which had been refrigerated at 0° gave a negative ferric chloride test for an enol, but solutions which had stood for about 7 to 9 days at room temperature gave a positive enol test. It is believed that the slow increase in color and the positive enol test are both indications that anthanol, the tautomer of anthrone, is gradually formed in the solution. Other decomposition products are undoubtedly formed also. For that reason, it is suggested that the 0.05% reagent be freshly prepared every three or four days.

RATE OF COLOR FORMATION

Determinations were made of the time required to reach the maximum color density after the reagent and solutions containing various concentrations of sucrose had been mixed. In these determinations, the sucrose solution was contained in one test tube and the reagent in another. At zero time the solutions were mixed by pouring the reagent into the sucrose solution and then pouring the mixture back into the first tube. Transmittancy readings were taken at frequent intervals until the reactions were substantially complete. In Figure 3 the optical density (—log transmittancy) is plotted against time after mixing. The transmittancies are the values relative to the transmittancy of the blank.

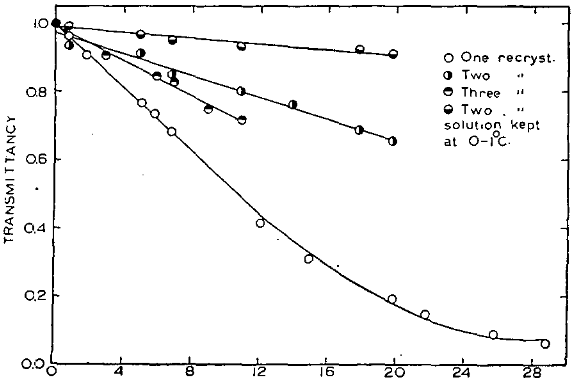

Figure 2. Effect of Recrystallization of Anthrone on Color Development in 0.05% Solutions

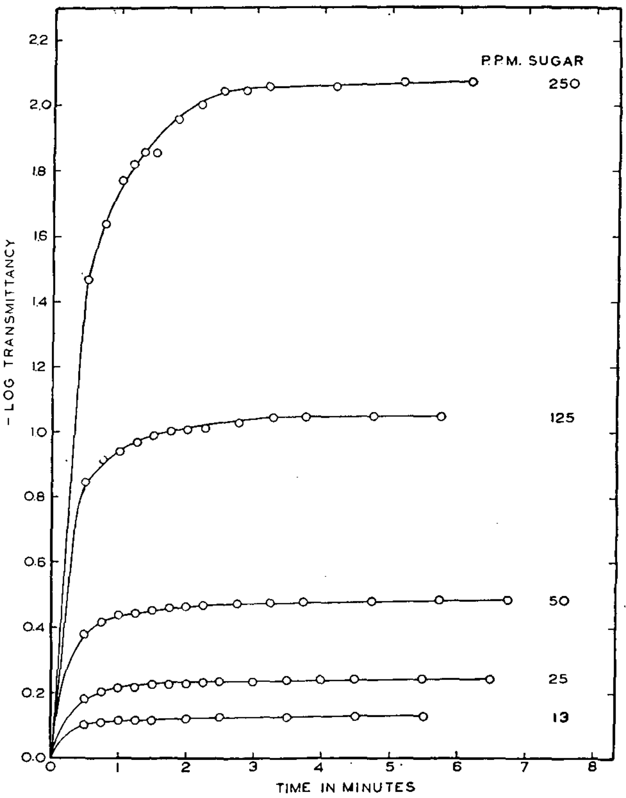

Figure 3. Rate of Color Development in Solutions of Anthrone Reagent and Sucrose

Table II. Rate of Color Development in Anthrone Test

Sucrose *P.p.m.*	Max. Density	Time to Reach 0.95 Max. Density *Min.*	Time to Reach 0.90 Max. Density *Min.*
250	2.07	1.8	1.4
125	1.05	1.5	1.0
50	0.49	2.1	1.1
25	0.24	1.8	1.1
12.5	0.13	1.8	1.1

Table II shows the time required to reach 90 and 95% of the final density. A delay of 2 minutes before measuring the color will ensure that 95% of the color has been developed, while about 90% is developed in 1 minute.

COMPARISON WITH α-NAPHTHOL TEST

The main advantage of anthrone is that it gives a more accurate and more sensitive test than α-naphthol. The coloring matter is distributed throughout the whole body of the solution and is not concentrated in a shallow ring. Furthermore, the extent of agitation of the tube has no effect on the test as it does with α-naphthol. Solutions containing 10 and 25 p.p.m. can be readily distinguished from each other. It is very difficult with the α-naphthol test to make this distinction.

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Colorimetric Determination of Iron with Nitroso-R-Salt

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The use of nitroso-R-salt for the spectrophotometric determination of iron has been studied critically. The effects of the following variables were determined: reagent concentration, pH, order of addition of reagents, time of reaction, iron concentration, and diverse ions. Under some conditions, the sensitivity of this reagent is much greater than that of 1,10-phenanthroline or 2,2′-bipyridine.

IN A recent study (*3*) of the use of nitroso-R-salt (1-nitroso-2-hydroxy-3,6-naphthalene disodium sulfonate) for the determination of iron in plant tissue, this reagent was compared to 1,10-phenanthroline and 2,2′-bipyridine. It compared favorably in sensitivity, and the green color was considered better suited to colorimetric measurement. With a 2.5-mm. cell the range was 0.2 to 50 p.p.m. A pH range of 8 to 10 and a filter with transmittancy limits of 445 to 505 mμ were suggested. In a more recent paper (*4*) it is stated that increased sensitivity is obtained using a filter with limits of 640 to 700 mμ.

Because of pH sensitivity, the color of the reagent, and the lack of information concerning interferences by diverse ions, a critical study of the use of this reagent was undertaken by means of a photoelectric spectrophotometer.

APPARATUS AND SOLUTIONS

Transmittancy measurements were made on a General Electric recording spectrophotometer set for a spectral band width of 10 mμ and on a Beckman DU spectrophotometer. Absorption cells 1.000 cm. thick were used, and pH was measured with a glass electrode assembly.

A stock iron solution containing 500 p.p.m. was prepared from reagent grade iron wire by dissolution in 10 ml. of sulfuric acid (specific gravity 1.84) and subsequent dilution to 1 liter. Solutions containing 100, 20, and 10 p.p.m. were prepared by dilution with redistilled water.

The reagent solution contained 0.5% nitroso-R-salt (Eastman No. 1124) and 30% redistilled (iron-free) acetone. A 10% solution of hydroxylamine hydrochloride was used as a reducing agent. For adjusting the pH, a 4 *M* solution of sodium acetate and 1.5 *M* solution of ammonia were made from reagent quality materials. The solutions containing the diverse ions were prepared from the nitrates for the cations and from the alkali metal salts for the anions. The solutions contained 10 ml. of diverse ion per ml.

COLOR REACTION

The reagent solution itself is yellow. A spectral transmittancy curve for 3 ml. of the 0.5% solution of nitroso-R-salt diluted to 50 ml. is shown in Figure 1. With ferrous iron, it forms a bright green complex with a transmittancy maximum at 550 mμ (see Figure 2). There is no transmittancy minimum within the visible range, but there is a broad band near 720 mμ. Figure 2 was obtained with the Beckman spectrophotometer, transmittancy values being determined each 10 mμ.

Since the Beckman instrument was not available during most of this work, the nature of the color reaction and the effect of various variables were studied with the General Electric instrument. Because this instrument is less sensitive at wave lengths above 640 mμ, transmittancy readings were taken at 620 mμ, which is in the wave-length range where the reagent itself does not absorb.

The effect of the following variables was determined by altering each one, independently, and maintaining all others constant. A final concentration of 1 p.p.m. of iron in a 50-ml. volume was used. In some cases the different variables are interdependent.

pH. Both the reagent and its complex with ferrous iron are sensitive to pH changes. As shown in Figure 1, below pH 5.35 the reagent is yellow and above pH 8.65 it is green. The intensity of the color due to the iron complex increases rapidly between pH 3.10 and 3.90. From pH 3.90 to 5.20, the variation in terms of iron concentration is well within the 2% error allowed for such work. Above pH 5.3 the intensity of the color again increases and the spectral transmittancy curve changes shape. That the decreased color formation at lower pH's can be attributed to a decreased rate of reaction is verified by comparison

Table I. Effect of pH on Rate of Color Development
(1 p.p.m. of Fe and 3.0 ml. of reagent in a volume of 50 ml.)

pH	Per Cent Transmittancy 20 minutes	4 hours
3.10	85.7	68.7
3.47	72.1	62.0
3.66	64.9	62.1
3.91	63.6	62.2
4.15	63.5	62.2
4.43	63.2	61.7
4.65	63.4	62.0
4.75	63.2	62.0
5.08	63.1	62.1
5.37	62.0	61.5

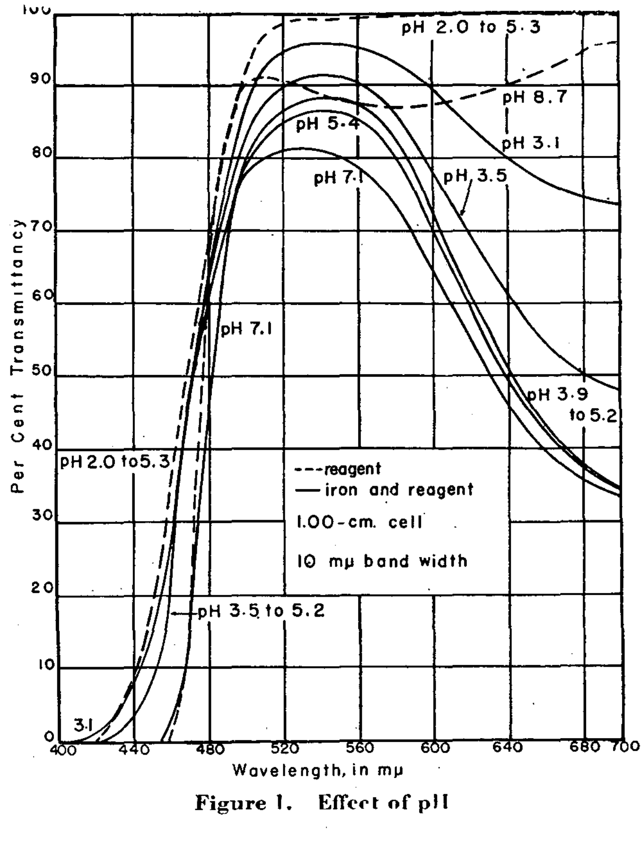

Figure 1. Effect of pH

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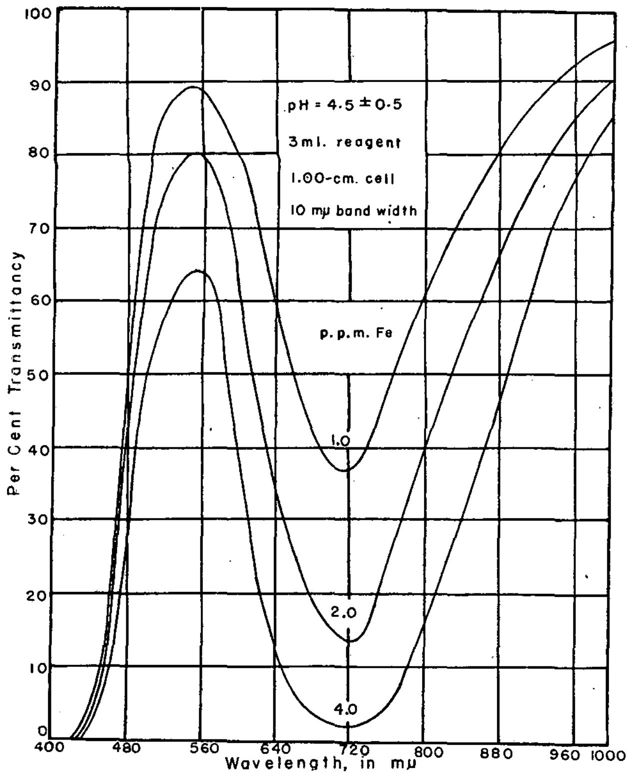

Figure 2. Effect of Iron Concentration

of the transmittancies taken from the freshly prepared solutions with those for the same solutions taken 4 hours later (Table I). Allowing a reasonable time for color development permits the use of the pH range 4.6 ± 0.5.

Concentration of Reducing Agent. If the amount of hydroxylamine hydrochloride is sufficient to reduce the iron completely, the transmittancy–wave-length curve is nearly independent of excess reductant. Such an excess of reducing agent seems to react with the color-forming reagent, but the effect is not sufficient to be significant.

Reagent Concentration. Eight-tenths milliliter of the reagent solution was required for complete color development of 1 p.p.m. of iron in a final volume of 50 ml. Too little reagent resulted in a curve of different shape. After standing for several hours, all the curves had the same shape as those usually obtained with an excess of reagent. During this time the transmittancy decreased in the wave-length range where only the reagent absorbs. One milliliter of reagent solution was sufficient for complete color development of 2 p.p.m. of iron. Thus, both the concentration and the quantity of reagent are significant in obtaining complete color development.

To obtain the iron complex in one form and to eliminate serious time effects, an excess of reagent must be used. Increasing the amount from the necessary excess to a larger excess has no effect between 520 and 700 mμ. However, between 400 and 520 mμ the reagent concentration is critical. This is one reason for the increase in the apparent sensitivity of the reagent with the use of the recently recommended filter (*4*) which transmits between 640 and 700 mμ.

Order of Addition of Reagents. During early experiments, in which 30 minutes were allowed for color development, changing the order of addition had no noticeable effect. However, later work revealed that the adjustment of pH before the addition of the reagent decreased the reaction rate. Consequently, the following sequence was adopted: iron, reducing agent, reagent, pH adjustment with ammonia, and sodium acetate.

Stability of Color. The relation of the stability of the colored system to the reagent concentration, the pH, and the order of addition of reagents has been discussed. The experimental work shows that the change in transmittancy at 620 mμ is equivalent to less than 2% iron after 6 hours, and to less than 5% iron after 48 hours, under the following conditions:

Use of the reagent sequence recommended above.
Allowance of a reaction period of 20 minutes after adjustment of pH.
Use of excess reducing agent and excess nitroso-R-salt.
Adjustment of pH between 3.9 and 5.2.
Measurement of transmittancy at some wave length between 550 and 640 mμ.

If a reaction period of 2 hours is allowed, a stable system is obtained. Otherwise, between 640 and 760 mμ the transmittancy increases significantly during the first 2 hours. Thus, if the transmittancy measurements are made within these limits, the longer reaction period is necessary.

Iron Concentration. The intensity of the green color is proportional to the concentration of ferrous iron. According to transmittancy readings taken at 620 and 720 mμ, the colored system conforms to Beer's law. At 620 mμ the range of concentration practical for a 1-cm. cell is 0.2 to 4.0 p.p.m. At 720 mμ the range is 0.05 to 2 p.p.m. If the increased sensitivity justifies the longer reaction period for a particular problem, and if the photocell in the instrument available is sensitive in this wave-length range, the latter wave length is preferable for study.

Diverse Ions. In order to determine the effect of diverse ions the following procedure was followed:

Five milliliters of a 10 p.p.m. standard iron solution were measured into a 50-ml. volumetric flask. To this were added 2.5 ml. of the diverse ion solution, containing 10 mg. of ion per ml. After the addition of 3 ml. of 10% hydroxylamine hydrochloride and 3 ml. of 0.5% nitroso-R-salt solutions, the pH was adjusted within the range 4 to 5 (glass electrode) with 1.5 *M* ammonia solution and 4 *M* sodium acetate. After 20 minutes, the solution was diluted to 50 ml. and the spectral transmittancy curve was taken. If interference equivalent to greater than 2% error in the iron concentration was observed, the quantity of diverse ion was decreased to find the permissible quantity. A 2% error corresponds to that allowed for similar methods.

Five hundred parts per million of the following ions may be present with 1 p.p.m. of iron without causing significant error; ammonium, cadmium, calcium, lead, lithium, magnesium, manganese, potassium, sodium, acetate, arsenate, arsenite, benzoate, borate, bromide, chlorate, chloride, iodate, iodide, lactate, nitrite, perchlorate, periodate, permanganate, salicylate, sulfate, sulfite, thiosulfate, tartrate, and thiocyanate.

Five hundred parts per million of aluminum, antimony, barium, bismuth, chlorostannate, chlorostannite, mercury (II), gold, silver, and chloroplatinate precipitate under the conditions found necessary for the satisfactory development of the color. The precipitation of the barium may be attributed to the formation of the sulfate (present in the standard iron solution) and that of the silver to the chloride (in the reducing agent).

Interference by ions which are soluble under the desirable conditions may be attributed to a variety of effects. Some ions absorb in the same portion of the spectrum as the iron complex and thus interfere. These are cerium (IV), chromium (III), chloroplatinate, dichromate, and uranyl ions. Metavanadate and molybdate ions, present as the sodium salts, were reduced to colored states.

Citrate, cyanide, fluoride, and oxalate greatly decrease the color formation, and formate and tungstate decrease it slightly. This effect is probably attributable to the formation of a colorless complex with the iron.

For reasons not apparent, 500 p.p.m. of beryllium, strontium, and orthophosphate increased the color development. Blanks indicated that this could not be attributed to contamination of the salts by iron.

Table II. Effect of Diverse Ions

Ion	Added as	Amount Present	Error	Amount Permissible
		P.p.m.	%	*P.p.m.*
Al^{+++}	$Al(NO_3)_3$	300	0	300
Be^{++}	$Be(NO_3)_2$	300	3	100
Ce^{++++}	$Ce(NH_4)_2(SO_4)_3$	10	2.5	5
Co^{++}	$Co(NO_3)_2$	1	3	0
Cr^{+++}	$Cr_2(SO_4)_3$	10	6	1
Cu^{++}	$CuSO_4$	1	8	0
Hg^{++}	$Hg(NO_3)_2$	100	2	100
Hg_2^{++}	$Hg_2(NO_3)_2$	500	10	200
Ni^{++}	$Ni(NO_3)_2$	2	5	0
Sr^{++}	$Sr(NO_3)_2$	200	2	200
Th^{++++}	$Th(NO_3)_4$	500	10	100
UO_2^{++}	$UO_2(C_2H_3O_2)_2$	300	3	100
Zn^{++}	$Zn(NO_3)_2$	200	5	40
CO_3^{--}	Na_2CO_3	100	2.25	50
$C_6H_5O_7^{---}$	$(HO)C(CO_2H)(CH_2CO_2H)_2$	500	62	100
CN^-	KCN	500	100	100
$PtCl_6^{--}$	K_2PtCl_6	100	16	10
$Cr_2O_7^{--}$	$K_2Cr_2O_7$	10	2	10
HCO_2^-	HCO_2Na	500	3	200
F^-	NaF	500	22	100
MoO_4^{--}	$(NH_4)_2MoO_4$	20	2.5	10
$C_2O_4^{--}$	$(NH_4)_2C_2O_4$	100	5	20
$H_2PO_4^-$	KH_2PO_4	500	3	300
$P_2O_7^{----}$	$Na_4P_2O_7$	5	2	5
SeO_4^{--}	Na_2SeO_4	500	4	300
WO_4^{--}	Na_2WO_4	100	6.5	20
VO_3^-	KVO_3	10	12	0

The presence of large quantities of mercury (I) or zinc changes the shape of the spectral transmittancy curve. The change is one that indicates the formation of a colored complex between these ions and the reagent. A blank on the zinc failed to verify this conclusion. Thus it is postulated that a small quantity of a colored complex is formed containing iron, zinc, and the reagent. Since a blank was not taken of the mercury, no conclusion can be reached. However, since the change in shape of the curve corresponds to that with zinc, the same explanation seems likely.

The quantitative results of such interferences and the permissible quantities are summarized in Table II. Spectral transmittancy curves for solutions containing typical interfering ions are shown in Figure 3.

DISCUSSION

Nitroso-R-salt is a satisfactory and sensitive reagent for the determination of ferrous iron. It has three major disadvantages: intense color of the reagent, sensitivity of both the reagent and the complex to pH changes, and time required for complete color development. The color of the reagent, along with the necessity for an excess, practically eliminates its use for visual comparisons. However, with the increasing use of photometric instruments, a region of the spectrum may be chosen where the reagent does not absorb. As the pH range for which the method is applicable is sufficiently broad, its control is not difficult. This restriction eliminates the determination of iron in the presence of several metallic ions which precipitate under prevailing pH conditions and necessitates the use of some method of checking the pH.

On the other hand, there are certain advantages, of which the following are probably most important:

The reagent is considerably cheaper and more easily available than 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′,2″-tripyridine.

If a photometer usable between 700 and 760 mμ is available, the sensitivity of this reagent is considerably greater than that for any of these other compounds in the visible region (*1*, *2*).

It compares favorably with other methods with respect to the effect of diverse ions. In some cases, higher concentrations of certain ions may be present.

RECOMMENDED PROCEDURE

Sample. Procure a representative portion of the material and subject it to the necessary preparative treatment to obtain either a neutral or acidic solution, free of ions which interfere with the color reaction. Measure a quantity to contain not more than 0.3 mg. of iron in a volume of 25 ml. or less.

Desired Constituent. Transfer the solution to a 50-ml. volumetric flask and add 3 ml. of a 10% hydroxylamine hydrochloride solution and 3 ml. of a 0.5% solution of nitroso-R-salt, containing 30% acetone. Adjust the pH within the range 4 to 5 with 1.5 *M* ammonia and 4 *M* sodium acetate. (This may be done easily by making the sample slightly acidic to litmus, using either 2 *M* hydrochloric acid or the ammonia; adding the reducing agent and reagent; and then adding 2.5 ml. of the 1.5 *M* ammonia and 0.5 ml. of the sodium acetate solution for a final volume of 50 ml.) After 20 minutes, dilute to volume and determine the transmittancy at 620 mμ, or use a filter with no transmittance outside the wave-length range 550 to 640 mμ. If greater sensitivity is required, allow the solution to stand for 2 hours before dilution and determine the transmittancy at a wave length between 640 and 720 mμ.

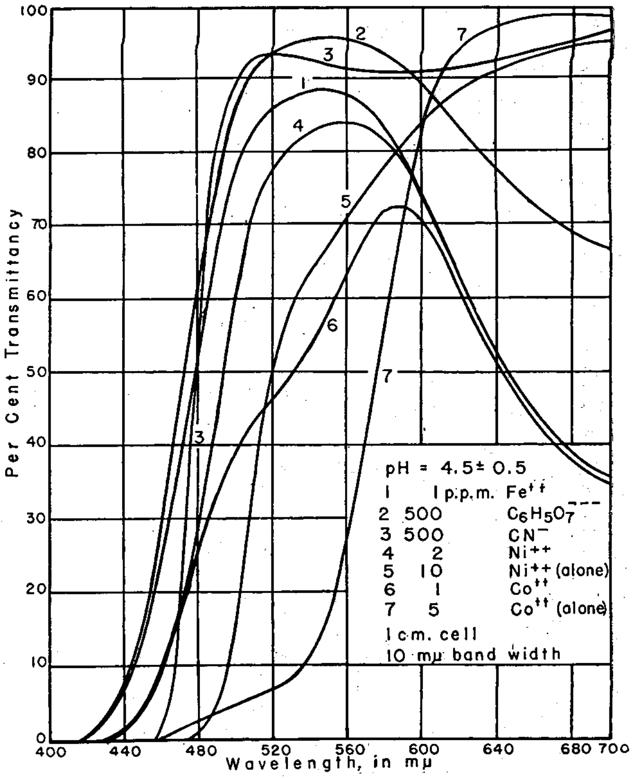

Figure 3. Effect of Diverse Ions

SUMMARY

Nitroso-R-salt for the determination of ferrous iron has considerable merit, although it does not equal such cyclic nitrogen compounds as 1,10-phenanthroline, 2,2′-bipyridine, and 2,2′-2″-tripyridine with respect to stability and freedom from pH effects. The pH must be maintained within the range 4 to 5. Under some conditions of color measurement it has considerably greater sensitivity than the other compounds mentioned. An excess of reagent must be added, a reaction period allowed to elapse, and transmittancy readings taken at a wave length at which the reagent does not absorb.

The effect of 67 ions on the color development has been studied. In this respect this reagent compares favorably with the cyclic nitrogen reagents for iron.

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Colorimetric Determination of Iron with Various Dioximes

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The application of several dioximes for the determination of iron has been studied. These include the new reagent diethylaminobutanedionedioxime, butanedionedioxime, and 1,2-cyclohexanedionedioxime. The colors obtained fade rapidly unless stabilized by an excess of sodium dithionite which reduces iron in ammoniacal solution. The new reagent may be stabilized with pyridine.

IN HIS first paper on 1,2-dioximes, Tschugaeff (*6*) reported that ferrous iron reacts with these compounds in the presence of ammonia, pyridine, or aliphatic amines to form soluble complexes whose colors vary from red to violet. Later Tschugaeff and Orelkin (*7*) suggested that butanedionedioxime (dimethylglyoxime) could be used for the colorimetric determination of iron. They reduced the iron with hydrazine sulfate and developed the color by heating before and after the addition of an excess of concentrated ammonia. A standard had to be prepared simultaneously and compared immediately.

Inasmuch as Diehl (*2*) pointed out the desirability of a critical study of this method with modern colorimetric technique, this work was undertaken. It seemed of interest to compare dioxime reagents with others used for determining iron.

APPARATUS AND SOLUTIONS

Transmittancy measurements were made on a General Electric recording spectrophotometer set for a spectral band width of 10 $m\mu$. Absorption cells 1.000 cm. thick were used, and measurements of pH were made with a glass electrode assembly.

A stock iron solution, containing 500 p.p.m., was prepared from reagent grade iron wire by dissolution in 10 ml. of sulfuric acid (specific gravity 1.84) and subsequent dilution to 1 liter. Solutions containing 100, 20, and 10 p.p.m. were prepared by dilution with water.

Three reducing agents were used: a 10% aqueous solution of hydroxylamine hydrochloride; a 10% aqueous solution of sodium dithionite (sodium hydrosulfite or hyposulfite, $Na_2S_2O_4$); and an ammoniacal dithionite solution consisting of 100 ml. of concentrated ammonia, 10 grams of sodium dithionite, and 50 ml. of water. Although the dithionite solutions were cloudy when first prepared, they cleared on standing a short time. However, their use while still cloudy gave clear solutions after reaction. The ammoniacal solution was serviceable for several days; but the other, because of rapid oxidation, had to be prepared every 2 hours.

Reagent quality 15 *N* ammonia, pyridine (Eastman Kodak Co.), and various primary amines, supplied by the Commercial Solvents Corporation, were used as bases.

One per cent ethanolic solutions were prepared of butanedionedioxime and diethylaminobutanedionedioxime. A 0.2% ethanolic solution of 1,2-cyclohexanedionedioxime (G. F. Smith Chemical Co.) was used. Diethylaminobutanedionedioxime is a new compound recently prepared by Bachman and Welton (*1*). All these reagent solutions were colored. Only the 1,2-cyclohexanedionedioxime shows any measurable absorption in the concentration found after dilution and this is not significant. This compound is said to have been perfectly white when bottled. However, at the time of use it was brown.

The solutions containing the diverse ions were prepared from the nitrates for the cations and from the alkali metal salts for the anions. These solutions contained 10 mg. of the diverse ion per ml.

STUDY OF TSCHUGAEFF'S METHOD

Two solutions were prepared containing a final iron concentration of 2 p.p.m. One was made exactly according to Tschugaeff's original procedure, with heating; the other was not heated. Only a very faint color developed in the first; a slightly deeper color appeared in the other one, but it soon faded to match the first. Previous work in this laboratory (*4*) showed that, for a given color-forming reagent, the reduction of iron with hydrazine sulfate gave a less intense color than with hydroxylamine hydrochloride. Since similar results were obtained with butanedionedioxime in the present work, it seemed preferable to attempt to stabilize the more sensitive but fleeting colored system rather than to study the weaker but apparently more stable system.

COMPARISON OF DIOXIMES

Before attempts to stabilize the iron-butanedionedioxime system were made, the reactions of the following compounds with ferrous iron were studied: diethylaminobutanedionedioxime, diphenylethanedionedioxime, di(2-furyl)ethanedionedioxime, and 1,2-cyclohexanedionedioxime. A strongly colored complex was obtained with all four dioximes in the presence of excess ammonia and hydroxylamine hydrochloride. The latter compound was used to reduce the iron in an acidic solution before adding the ammonia. The complexes with diphenylethanedionedioxime and di(2-furyl)ethanedionedioxime faded so rapidly that readings were not taken. Under these conditions, none of these systems is sufficiently stable to be used for colorimetric measurement of iron. A method of stabilization was sought in the hope that it might make one or more of them suitable for the quantitative determination of iron.

STABILIZATION OF COLORED SYSTEM

According to Diehl (*2*), the formulas of the ferrous-dioxime complexes correspond to the general formula $Fe(DH_2)_2A_2$, in which DH_2 represents a molecule of the dioxime and A a molecule of ammonia, pyridine, or primary amine. The instability of the colored system is attributed to the ease with which iron is oxidized to the ferric state by the oxygen of the air in the presence of ammonia. These two facts indicate two methods of stabilization: the substitution of pyridine or a primary amine for ammonia; or the use of an excess of an agent which reduces iron in an ammoniacal solution (*5*).

Table I. Effect of Various Bases on Absorption Maxima

Oxime	Pyridine, $m\mu$	Ammonia, $m\mu$	*n*-Butylamine, $m\mu$
Butanedionedioxime	512	529	535
Diethylaminobutanedionedioxime	527	541	543
1,2-Cyclohexanedionedioxime	531	543	550
Diphenylethanedionedioxime	Cloudy	567	574

The following amines were studied: isobutylamine, *sec*-butylamine, *n*-butylamine, isoamylamine, and *n*-amylamine. Pyridine was included. The entire series was used with butanedionedioxime and diethylaminobutanedionedioxime. Visual comparison showed that only pyridine, *n*-butylamine, and *n*-amylamine had a stabilizing effect. Spectrophotometric study revealed that the effect of the two amines was insufficient, but pyridine appeared promising.

The shift of the absorption maxima toward other wave lengths, which accompanied variations in the type and amount of base, may be evidence of the inclusion of the base in the formula of the

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complex. These maxima are given for several dioximes with pyridine, ammonia, and *n*-butylamine in Table I.

In order to determine the validity of the suggestion that the oxidation of the ferrous iron is responsible for the instability of these colored systems, a faded solution was acidified, reduced, and made ammoniacal again. Visual comparison revealed that the characteristic color returned.

The following reducing reagents were tested by introducing small portions of the solids into the iron solution before the addition of diethylaminobutanedionedioxime and base: sodium sulfite, sodium thiosulfate, sodium nitrite, sodium dithionite, hydrazine sulfate, hydrazine chloride, hydroxylamine hydrochloride, and ascorbic acid. The use of sodium sulfite, sodium nitrite, and sodium thiosulfate resulted in little color development. After a reaction period of 10 minutes, the sodium dithionite gave a stable and sensitive colored system. The colors developed with hydrazine sulfate, hydrazine chloride, and hydroxylamine hydrochloride were satisfactory if the reduction was carried out in an acidic solution. Ascorbic acid reduced the iron, even if added to the ammoniacal solution. Since very few compounds reduce iron in ammoniacal solution, it is possible that this reaction might be developed into a colorimetric method for ascorbic acid.

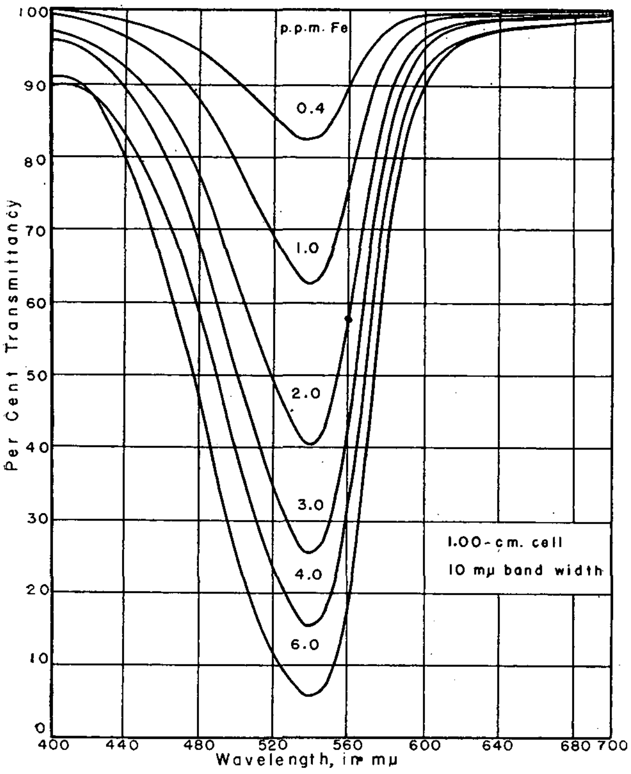

Figure 1. Effect of Iron Concentration with Diethylaminobutanedionedioxime

Sodium dithionite also stabilized the butanedionedioxime and the 1,2-cyclohexanedionedioxime systems but did not improve the stability of the iron complexes of the other dioximes.

A stable colored system is formed between ferrous iron and diethylaminobutanedionedioxime or butanedionedioxime in the presence of pyridine. However, a 40-minute reaction period is required. With sodium dithionite as reducing agent, a stable system is formed in the presence of ammonia with diethylaminobutanedionedioxime, butanedionedioxime, or 1,2-cyclohexanedionedioxime. Since only a 10-minute reaction period is necessary in this case, the ammonia method is recommended. Sodium dithionite gives slightly greater sensitivity also.

In order to determine the effect of the variables noted below (except No. 6), a final volume of 50 ml. was chosen, with a concentration of 2 p.p.m. of iron. Each variable was changed systematically while holding the others constant.

1. **Reducing Agents.** Sodium dithionite was added as the solid, as a 10% aqueous solution, or as the ammonia-stabilized system. Use of the solid eliminated frequent preparation of a solution and increased both the rate of reaction and the stability. This is recommended if an iron-free product can be obtained. Attempts to eliminate the iron by Hill's method (*3*) were unsuccessful. A 10% aqueous solution was so instable that it had to be prepared hourly. In routine work the ammoniacal solution was used. A blank solution in the back beam of the spectrophotometer eliminated the effect of the contaminating iron.

2. **Ammonia Concentration.** For the diethylaminobutanedionedioxime complex the effects of the ammonia and of the sodium dithionite were studied separately. Variation from 0.5 to 2.0 ml. of ammonia shifts the wave length of the minimum and increases the color formed. Spectral transmittancy curves for solutions containing 2 to 4 ml. of ammonia coincide.

3. **Reductant Concentration.** With diethylaminobutanedionedioxime 1.5 ml. of the ammoniacal reducing agent are necessary for complete color development; 2 ml. are necessary with butanedionedioxime. Addition of 6 ml. results in no greater color. With 1,2-cyclohexanedionedioxime, 6 ml. of ammoniacal reducing agent are required. Up to 8 ml. may be added.

4. **Color-Former Concentration.** For complete color development with 2 p.p.m. of iron, 0.5 ml. of 1% butanedionedioxime or diethylaminobutanedionedioxime is sufficient. One milliliter of the 0.2% 1,2-cyclohexanedionedioxime is required. A reasonable excess of any of these reagents does not interfere.

5. **Order of Addition of Reagents.** The first study of this variable was made with the diethylaminobutanedionedioxime, using the 10% sodium dithionite solution and 15 *N* ammonia. The color developed is decreased slightly if the addition of the ammonia precedes the reductant. This result was attributed to a decreased rate of reaction. With the ammoniacal reducing reagent, the sequence of adding the reactants is not critical for either butanedionedioxime or its derivative; but with 1,2-cyclohexanedionedioxime complete color development was achieved only by following the order iron, reducing agent, and the color-forming reagent.

6. **Iron Concentration.** The colored system obtained with each of the dioximes studied obeys Beer's law through the range of concentration investigated. Spectral transmittancy curves for diethylaminobutanedionedioxime are shown in Figure 1. Those for butanedionedioxime and 1,2-cyclohexanedionedioxime are similar, with minima at 529 and 543 mμ, respectively. With 1-cm. cells all three are applicable in concentrations ranging from 0.4 to 6.0 p.p.m. The sensitivity of butanedionedioxime is slightly less than that of the other two.

7. **Stability of Colored System.** Because of the time effects observed in preliminary work with these dioximes in studying other variables, a 10-minute period was allowed for the color-forming reaction before final dilution. With the procedure described below, this reaction period was then varied from 5 to 20 minutes. Readings of the transmittancy maxima, taken immediately after dilution, are the basis of the following recommendations: (*a*) a reaction period of 15 minutes is necessary for complete color development with any of the three reagents; if an accuracy within 2% is acceptable, this period may be decreased to 5 minutes; (*b*) transmittancy readings must be taken within 30 minutes after dilution for butanedionedioxime or diethylaminobutanedionedioxime, and within 15 minutes for 1,2-cyclohexanedionedioxime.

8. **Diverse Ions.** In order to determine the effect of various diverse ions, the following procedure was followed:

Five milliliters of an iron solution, containing 20 p.p.m., were measured into a 50-ml. volumetric flask. To this were added 2.5

ml. of the diverse ion solution, containing 10 mg. of the ion per ml. After the addition of 3 ml. (6 ml. with 1,2-cyclohexanedionedioxime) of the ammoniacal sodium dithionite solution, the requisite quantity of one of the dioxime reagents was added. After 15 minutes had elapsed, the solution was diluted to final volume and the transmittancy readings were taken at the respective absorptance maxima. Complete curves were recorded only if a change of hue was noticed, or if a large and unexpected interference occurred. If interference equivalent to more than 2% error in the amount of iron present was observed, the quantity of interfering ion was decreased to find the amount which could be tolerated without exceeding 2% error. Typical spectral transmittancy curves for selected ions are shown in Figure 2 for diethylaminobutanedionedioxime.

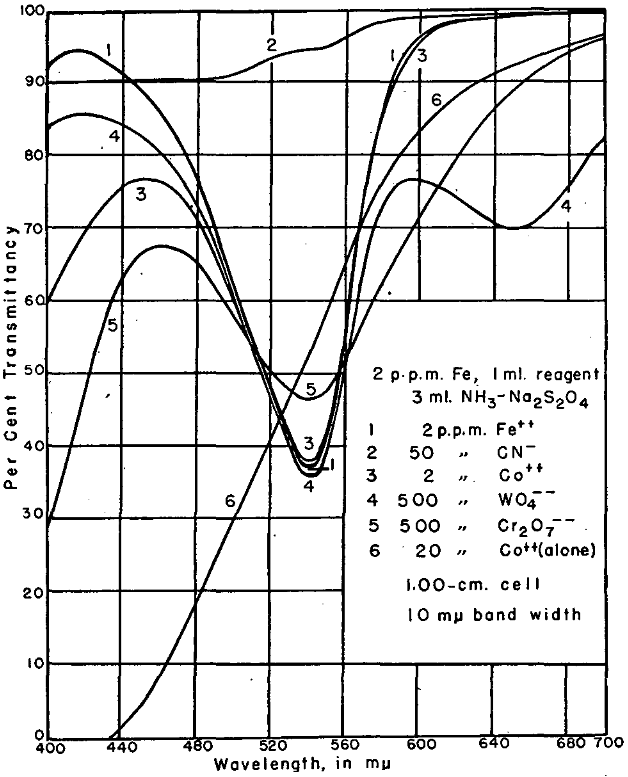

Figure 2. Effect of Diverse Ions with Diethylaminobutanedionedioxime

The effect of 68 ions on the formation of a colored system formed between iron and diethylaminobutanedionedioxime was studied. The errors noted and the quantities permissible to hold the error within 2%, for those ions which exhibited significant interference, were determined.

Five hundred parts per million of the following ions may be present with 2 p.p.m. of iron without causing significant error: ammonium, lithium, potassium, sodium, arsenate, borate, bromide, chlorate, chloride, iodide, lactate, molybdate, nitrate, oxalate, perchlorate, pyrophosphate, salicylate, sulfate, sulfite, tartrate, thiocyanate, or thiosulfate.

Because of the necessity for excess ammonia for the development of the color, most of the common metals precipitate. Aluminum, beryllium, chromium (III), cerium, gold, magnesium, manganese, thorium, uranyl, chlorostannate, chlorostannite, permanganate, and selenate ions precipitate in the presence of the required concentration of ammonia. The insoluble sulfates of barium, calcium, lead, and strontium are formed. Sodium dithionite reduces the following ions to the metallic state under the conditions of color development: antimony, bismuth, mercury (I and II), and silver. As would be expected, copper and nickel form insoluble compounds with the reagent.

The separation of nickel from most metals with butanedionedioxime, under similar pH conditions, is a standard laboratory and industrial analytical procedure. This is accomplished by the addition of an excess of ammonium chloride and tartaric acid. The addition of 2 ml. of 10% aqueous solutions of each of these, in a final volume of 50 ml. containing 2 p.p.m. of iron did not interfere with color development. Five hundred parts per million of aluminum, manganese, or thorium remained in solution under these conditions. Although the aluminum did not interfere, the solutions containing thorium or manganese failed to give complete color development. Beryllium, cerium, and chromium (III) precipitated.

Uranyl, dichromate, and chloroplatinate ions interfered because of their own colors.

A low concentration of cobalt forms a weak brown color by reaction with the reagent. The metal likewise reacts with the ammoniacal dithionite solution to give a much deeper color.

Decreased color development was caused by acetate, arsenate, benzoate, carbonate, cyanide, formate, and iodate. This effect is attributed to the formation of an iron complex by these ions.

The only interpretation of the interference of cadmium, manganese, thorium, and zinc is the formation of a colorless complex with the reagent.

Addition of sodium metavanadate to the iron solution produced a yellow solution. Subsequent addition of the reductant and color-forming reagent changed only the shape of the transmittancy curve. A hue change was produced on adding sodium tungstate to an iron solution. In this case, experiment showed that a blue hue resulted from reduction of some complex of iron and tungsten, in the absence of any dioxime.

Complete diverse ion studies were not made for butanedionedioxime and 1,2-cyclohexanedionedioxime, but interferences caused by 20 selected ions are compared in Table II for all three reagents.

There is little basis for the recommendation of one of these dioximes over the other. The sensitivity of 1,2-cyclohexanedionedioxime and of diethylaminobutanedionedioxime is slightly greater than that of butanedionedioxime. The first is slightly less stable. Diethylaminobutanedionedioxime is the only one which is applicable when stabilized with pyridine.

These reagents compare favorably in sensitivity with such well-known reagents as 1,10-phenanthroline and 2,2′-bipyridine. Their iron complexes, however, are inferior in stability, and such drastic conditions are required for color development that all the common cations except the alkali metals and ammonium interfere, either because of precipitation or reaction.

However, the reagents can be obtained easily and should have

Table II. Comparison of Effect of Diverse Ions on Various Dioximes

Diverse Ions	Concn., P.P.M.	Per Cent Error Butanedione-dioxime	 Diethylamino-butanedione-dioxime	 1,2-Cyclohex-anedionedioxime
Co^{++}	5	−15	+ 5	+ 5
Cu^{++}	5	−12.5	[a]	+13
Cd^{++}	200	− 4	− 2	− 4
UO_2^{++}	10	− 1	− 2	0
AsO_3^{--}	200	−34	− 2	−44
$C_2H_3O_2^-$	500	− 5	− 5.5	− 1
$C_7H_5O_2^-$	200	− 0.5	0	0
$B_4O_7^{--}$	500	− 2	− 5	0
CO_3^{--}	100	− 5.5	− 2	− 1
$C_6H_5O_7^{---}$	500	+ 0.5	− 4.5	0
Cr^{+++}	20	−12	−62	−20
$Cr_2O_7^{--}$	10	+ 0.5	− 6	− 0.5
F^-	500	− 6.5	− 4	− 3.4
IO_3^-	50	−11	− 4	0
IO_4^-	50	− 4.5	− 4	− 0.5
NO_2^-	100	− 0.5	−10.5	− 0.5
$H_2PO_4^-$	100	− 1	0	− 5.5
VO_3^-	100	− 7	− 1	−15

[a] Precipitation occurs with 20 p.p.m. Cu^{++}.

some specific applications for the determination of iron in solutions of high pH.

RECOMMENDED PROCEDURE

Sample. Procure a representative portion of the material and subject it to the necessary preparative treatment. By weight or volume, measure the quantity of sample which contains not more than 6 mg. of iron. Dissolve the sample, if necessary, by appropriate means. Remove those substances which precipitate at pH's greater than 9.5 and check the interference of other ions present. Dilute to 100 ml.

Desired Constituent. To a 50-ml. volumetric flask containing a 5-ml. aliquot of the sample, add 3 ml. of the reducing agent (the reducing agent is prepared by dissolving 10 grams of sodium dithionite in 100 ml. of concentrated ammonia and 50 ml. of water. Use of 0.1 to 0.4 grams of the solid sodium dithionite and the subsequent addition of 2 ml. ammonia is more desirable, if an iron-free salt is available) and 0.5 ml. of 1% butanedionedioxime or diethylaminobutanedionedioxime. (Two milliliters of a 0.2% ethanolic solution of 1,2-cyclohexanedionedioxime may be substituted if 6 ml. of the ammoniacal dithionite are used, and if transmittancy readings are taken at 543 $m\mu$.) Allow this to stand for 15 minutes, dilute to volume, and take the transmittancy reading at 529 $m\mu$ for the former and 541 $m\mu$ for the latter reagent. A 30 $m\mu$ spectral band, with these wave lengths at the center, may be used. A method of visual comparison may be used, since these systems obey Beer's law.

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Spectrophotometric Evaluation of the Color of Ink Marks on Paper

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A spectrophotometric procedure has been developed for evaluating the color of marks made on white paper by several types of ink. Data are presented on the colors resulting when inks of a wide range of color are applied to a definite kind of paper in specified concentrations. Specifications may be given in terms of tristimulus values, trichromatic coefficients for the graphical plotting of chromaticity, and dominant wave length, luminance, and purity.

ALTHOUGH man has used writing ink for centuries, he has made few attempts to evaluate, in other than vague and qualitative terms, the appearance which the ink leaves on paper. Descriptive terms such as "blue black," "jet black," "red," and the like have long been in common usage; while capable of conveying a general impression, they furnish no exact information.

One of the few proposals for putting the description of ink colors on a rational basis was made more than forty years ago by Lovibond (*8*), who expressed the need of "workers in colour (for) . . . . a system of measuring and recording the colour changes as they occur." Lovibond exposed samples of various materials, including writing ink marks on paper, to several conditions, including north daylight, south daylight, and north daylight in a damp atmosphere. His system of measurement employed transparent colored glass standards.

In more recent years, colorimetry based on spectrophotometry has provided a quantitative means of color evaluation in which the color description, definition, or specification is stated in terms of fundamental units. An especially lucid and valuable exposition has been given by Hardy (*6*).

The spectrophotometric method has been utilized to supply a wealth of information on a wide variety of colored materials, including dyes (*2, 3, 7, 10, 11, 12*) and printing inks (*5, 6*), but does not appear to have found previous application in the field of writing inks.

In the present work, a number of inks chosen to represent different ink types were applied to white paper in concentrations typical of handwriting. The spectrophotometer requires a sample about 3.75 to 5 cm. (1.5 to 2 inches) in diameter. In order to prepare such samples, it was necessary first to determine the volume of ink to be put on a given area of paper. Spectral reflectance curves were prepared and the resulting data were used to calculate the tristimulus values (X, Y, Z), the trichromatic coefficients (x, y), and the factors, dominant wave length, luminance, and purity. These factors correspond closely to the psychological attributes of hue, value, and chroma, respectively, as used, for example, in the Munsell (*9*) system of color notation. This procedure gave precise definition to the colors resulting from the application to paper of a considerable variety of inks. The results of this survey are presented in Table I.

EXPERIMENTAL

Paper. Hammermill Ledger paper weighing 30.5 pounds (14 kg.) per 500-sheet ream, 17 × 28 inches (42.5 × 70 cm.), substance 24, was used throughout.

Ink Samples. Commercial inks were purchased on the open market and taken randomly from the shipping stocks of the authors' employer. Experimental inks were prepared in the laboratory.

Ink Concentration of Handwriting. The amount of ink laid down on the paper during ordinary writing will vary between pens and also between individuals. In a sense, then, there is no such thing as "normal" writing. Nevertheless, experiment showed that 0.001 ml. of ink per sq. cm. of paper surface represents a value well within the normal range; the ink concentration sometimes falls below this value and occasionally may be more than 0.002 ml. of ink per sq. cm. To determine these values, straight lines were drawn. Their lengths were measured macroscopically and their average widths microscopically. These data, together with information on the amount of ink consumed as determined by weighing the pens before and after use, permitted the calculation of ink laid down per unit area. Several individuals participated in drawing the lines, and pen nibs from extra fine to stub were used. A number of precautions were used, including the use of rubber gloves for handling the pens.

Approximations were adequate, as it was sufficient to make certain that ink concentrations on the samples prepared for spectrophotometric work were not outside the range of handwriting. The concentrations determined are in good agreement with those reported by Brecht and Liebert (*1*).

Preparation of Ink Marks on Paper. Ink concentration is indicated in Table I; in most cases it was 0.001 ml. per sq. cm., although 0.002 ml. per sq. cm. was used in a few experiments.

The desired volume of ink was transferred from a pipet to a glass rod. The rod was used to spread the ink evenly on a 5-cm. square which previously had been delineated accurately on paper with wax crayon.

Spectral Reflectance Curves. Each ink mark was allowed to air-dry for one hour before being placed in the spectrophotometer for the drawing of the curve. Where it was desired to study the effect of aging on color, further curves were prepared from the same part of the mark after appropriate intervals. Magnesium oxide was used as a comparison standard, and the samples were backed with black velvet.

Marks were made and spectral reflectance curves were prepared by the Electrical Testing Laboratories, 2 East End Ave. at 79th St., New York, N. Y. A General Electric automatic recording spectrophotometer was used.

A few curves are shown in Figures 1 and 2.

Calculation. The calculations giving the numerical values were carried out as outlined by Hardy (*6*), using the data for I.C.I. Illuminant C. This light source and these data were adopted by the International Commission on Illumination in 1931 as best representing average daylight. Ten selected wave lengths for Illuminant C were used for the relatively flat curves obtained from black ink marks and white paper; thirty selected wave lengths were used in all other cases.

Table I. Spectrophotometric Data on Marks Made with 21 Writing Inks

Sample	Brand	Time from Sample Preparation to Drawing of Curve	Trichromatic Coefficients x	Trichromatic Coefficients y	Dominant Wave Length, mμ	Luminance (*Y*), %	Purity, %
	Washable Inks						
1	Sheaffer's Skrip washable blue	1 hour	0.228	0.214	473	24.4	42.2
1		24 hours	0.227	0.213	473	24.7	42.7
1		1 week	0.229	0.211	472	24.8	42.3
1		2 weeks	0.229	0.213	473	24.4	42.0
2[a]		1 hour	0.208	0.183	472	17.2	53.7
3	Sheaffer's Skrip washable black	1 hour	0.298	0.324	499	18.6	4.0
3		24 hours	0.302	0.315	490	18.8	3.1
3		1 week	0.301	0.313	487	19.2	3.7
3		2 weeks	0.302	0.314	487	19.1	3.2
4		1 hour	0.290	0.301	481	8.6	9.0
5	Sheaffer's Skrip washable purple	1 hour	0.257	0.210	447	26.7	35.2
5		24 hours	0.254	0.206	450	26.2	36.8
5		1 week	0.256	0.204	441	26.0	36.8
5		2 weeks	0.258	0.209	442	26.6	35.2
6[a]		1 hour	0.246	0.179	435	18.1	44.7
7	Sheaffer's Skrip emerald green	1 hour	0.270	0.376	510	46.5	13.7
8	Sheaffer's Skrip washable brown	1 hour	0.380	0.361	584	34.3	30.7
9	Sheaffer's Skrip peacock blue	1 hour	0.222	0.280	486	41.7	36.0
10	Sheaffer's Skrip Persian rose	1 hour	0.352	0.252	511c[b]	28.7	33.7
11	Sheaffer's Skrip melon red	1 hour	0.410	0.302	493c[b]	34.3	24.3
	Blue-Black Inks, Permanent						
12	Sheaffer's Skrip permanent blue-black[c]	1 hour	0.254	0.260	477	27.7	26.9
12		24 hours	0.253	0.259	477	27.4	27.2
12		1 week	0.252	0.257	477	27.7	28.0
12		2 weeks	0.254	0.258	477	27.3	27.1
13	Sheaffer's Skrip permanent blue-black[c]	1 hour	0.246	0.268	481	26.4	28.5
13		24 hours	0.252	0.259	478	27.1	27.6
13		1 week	0.252	0.258	478	27.1	27.8
13		2 weeks	0.253	0.257	477	26.5	27.7
14	Sheaffer's Skrip permanent blue-black[c]	1 hour	0.253	0.265	479	25.9	26.4
14		24 hours	0.249	0.255	478	25.8	29.2
14		1 week	0.250	0.251	476	25.6	29.4
14		2 weeks	0.256	0.253	475	25.6	27.4
15	Sheaffer's Skrip permanent blue-black[c]	1 hour	0.256	0.268	479	27.7	25.1
15		24 hours	0.252	0.260	478	27.4	27.5
15		1 week	0.253	0.257	477	27.4	27.6
15		2 weeks	0.254	0.258	477	27.2	27.1
16[a]		1 hour	0.227	0.216	474	13.6	42.2
17	Parker's Quink permanent blue-black	1 hour	0.251	0.268	480	26.0	26.8
17		24 hours	0.251	0.264	479	22.0	27.2
17		1 week	0.253	0.262	478	21.6	26.8
17		2 weeks	0.255	0.267	479	21.7	25.7
18[a]		1 hour	0.215	0.229	479	17.2	44.5
19	Carter's Midnight blue-black permanent	1 hour	0.245	0.259	479	24.2	30.0
19		24 hours	0.255	0.258	477	22.1	26.9
19		1 week	0.252	0.254	476	22.1	28.2
19		2 weeks	0.255	0.258	477	22.1	26.9
20[a]		1 hour	0.220	0.213	475	14.6	45.0
21	Sanford's Penit permanent blue-black	1 hour	0.239	0.271	483	28.3	30.5
21		24 hours	0.242	0.266	482	23.1	30.2
21		1 week	0.244	0.262	480	21.6	30.0
21		2 weeks	0.247	0.266	481	20.5	28.4
21		4 weeks	0.248	0.267	481	19.9	28.0
22[a]		1 hour	0.209	0.236	481	20.5	45.6
23	Waterman's Ideal blue-black	1 hour	0.258	0.282	483	34.2	22.8
23		24 hours	0.262	0.272	479	27.2	22.5
23		1 week	0.263	0.270	478	25.1	22.4
23		2 weeks	0.266	0.274	478	24.3	20.8
23		4 weeks	0.266	0.275	479	24.5	20.8
24[a]		1 hour	0.228	0.240	479	24.4	38.4
25	Federal Specification TT-I-563a[d]	1 hour	0.255	0.267	479	25.7	25.6
25		24 hours	0.254	0.255	476	19.9	27.6
25		1 week	0.258	0.254	474	18.8	26.4
25		2 weeks	0.259	0.263	477	18.8	24.8
25	(Sample soaked in water 24 hours)	4 weeks	0.305	0.311	478	31.8	2.6
26[a]	Federal Specification TT-I-563a	1 hour	0.216	0.205	474	18.9	47.5
	Other Permanent Inks						
27	Sheaffer's Skrip permanent royal blue	1 hour	0.240	0.236	475	25.3	35.0
27		24 hours	0.240	0.238	476	25.6	34.7
27		1 week	0.239	0.233	475	25.2	35.8
27		2 weeks	0.242	0.238	475	25.8	34.0
28	Sheaffer's Skrip permanent jet black	1 hour	0.309	0.310	560c[b]	17.4	2.3
28		24 hours	0.309	0.311	560c[b]	16.9	2.0
28		1 week	0.306	0.306	566c[b]	17.2	3.3
28		2 weeks	0.307	0.307	565c[b]	17.1	3.2
29	Parker's Quink permanent black	1 hour	0.273	0.286	480	15.6	16.8
30	Carter's Midnight black permanent	1 hour	0.296	0.300	475	20.6	7.1
31	Sheaffer's Skrip permanent red	1 hour	0.375	0.332	596	46.2	21.6
31		24 hours	0.379	0.334	596	45.9	23.3
31		1 week	0.375	0.331	597	47.0	21.4
31		2 weeks	0.377	0.332	597	46.4	22.1
32	Experimental permanent jet black	1 hour	0.298	0.312	487	14.9	4.7
33	Experimental permanent red	1 hour	0.435	0.302	687	29.9	29.6
	Paper						
34	Hammermill Ledger paper	..	0.311	0.319	564	71.6	1.0

[a] Concentration of ink on paper was 0.002 ml. per sq. cm.; 0.001 ml. per sq. cm. in all other cases.
[b] Represents purple; dominant wave length indicated is that wave length which is complementary to purple.
[c] Quadruplicate samples.
[d] Not a commercial ink; this formula serves as federal standard for writing ink (*4*).

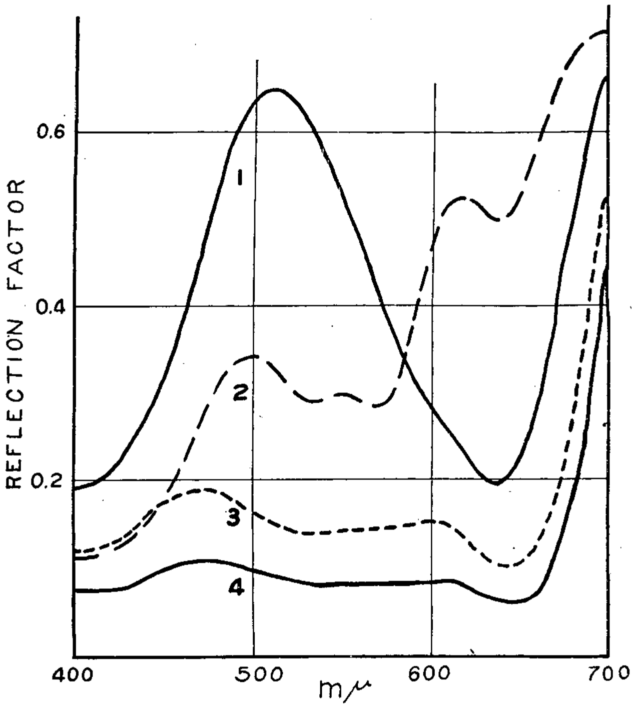

Figure 1. Marks Made with Washable Inks of Several Colors

		Ml./sq. cm.
1.	Emerald green	0.001
2.	Brown	0.001
3.	Black	0.001
4.	Black	0.002

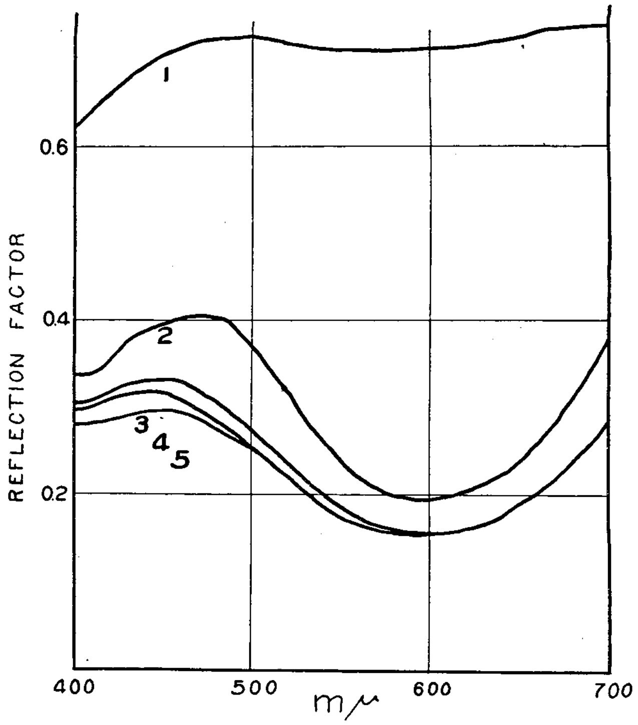

Figure 2. Effect of Aging on Mark Made with Iron Tannate Ink

0.001 ml. of ink per sq. cm.

1.	White paper	
2.	Federal speci-	1 hour
3.	fication ink,	24 hours
4.	TT-I-563a	1 week
5.		2 weeks

DISCUSSION OF DATA

The data presented give fundamental specifications of the colors resulting when inks of a wide range of color are applied to a specified kind of paper in specified concentrations. The specifications may be given in terms of: (*a*) X, Y, and Z; (*b*) x and y for the graphical plotting of chromaticity, and the luminance, Y; (*c*) dominant wave length, luminance, and purity.

The purpose of conducting parallel experiments on quadruplicate marks made with one of the inks was to study reproducibility of results. Since only minor variations were observed from sample to sample, it was concluded that the method of application was satisfactory.

The authors were particularly interested in studying the changes resulting from aging. Marks made with washable inks remained substantially constant during the period investigated. This result is not surprising, since this class of inks consists essentially of dyes dissolved in water. Permanent inks, in addition to dyes, usually contain iron tannate or other metallic complex to provide permanence, though in a few inks direct dyes are used to confer this property. The data show that marks made with representatives of the permanent class vary greatly in their behavior toward aging. Some acquire their maximum lightness contrast in at most one hour after preparation, nor does aging appreciably change the dominant wave length and purity. Other inks give marks which change slightly, while still others give marks which undergo profound changes. In such cases, although there is little change in dominant wave length and possibly a slight decrease in purity, the aging process leads to the phenomenon commonly called "darkening" as is evidenced by a large decrease in luminance. In some instances, more than two weeks elapse before minimum luminance is attained.

Black ink presents a special case, for good neutrality of color depends on low (or ideally zero) purity. Maximum contrast is given by minimum luminance. Dominant wave length merely gives the direction of departure from neutrality.

This method of color specification should be useful for many other ink studies—for example, as a means of measuring the resistance of ink marks to deteriorating influences such as light energy or water soaking. As an illustration, data pertaining to a mark made with Federal Specification Ink TT-I-563a (*4*) and later soaked in water are included in Table I.

ACKNOWLEDGMENT

The authors wish to express their thanks to the W. A. Sheaffer Pen Company for permission to publish these results.

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Improved Procedure for Determination of Aldehydes

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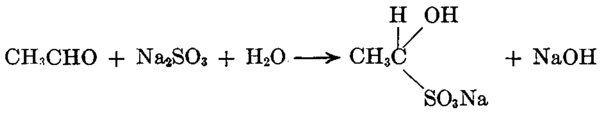
This procedure provides a means for determining aldehydes, without difficulties of equilibrium or end point, by forming the corresponding bisulfite addition product in a sodium sulfite–sulfuric acid mixture. The excess acid is titrated potentiometrically. Plotting a graph of pH *vs.* milliliters of standard alkali yields results, on the average, reproducible to ±0.2%. Titrating to the predetermined pH for the end point yields results good to ±0.4%. Ketones generally do not interfere if present in amounts less than 10 mole %. Acetals are not attacked by the reagents and do not interfere in the analysis.

THE fact that aldehydes add bisulfite has been known for many years and has been used as the basis for analytical methods for determination of aldehydes. Ripper's method, in which (*5*) aldehydes react with bisulfite and excess bisulfite is determined by iodine oxidation, has undergone much modification. Parkinson and Wagner (*4*) sum up the iodometric methods for determining excess bisulfite and also give methods for overcoming some difficulties in earlier procedures.

The iodometric methods require standardization of the bisulfite solution each day because of the instability of the solution, and difficulties with the equilibrium between aldehyde and bisulfite *vs.* aldehyde bisulfite addition product sometimes affect results. As the iodine consumes excess bisulfite, the addition product dissociates back to free aldehyde and bisulfite. The extent of the error depends on the equilibrium constant for the particular aldehyde, the amount of bisulfite addition product present, the amount of iodine present, and the time it is in the solution.

The determination of increase in alkalinity in the system where aldehydes react with sulfite has been used to determine aldehydes. However, the existing methods exhibit difficulties of equilibria and end point. Seyewetz and Bardin (*7*) used this type of approach in the determination of acetaldehyde; acetaldehyde reacted with sodium sulfite and the sodium hydroxide formed was titrated with standard acid.



$$CH_3CHO + Na_2SO_3 + H_2O \longrightarrow CH_3C(H)(OH)(SO_3Na) + NaOH$$

However, there is an equilibrium involved, and the reverse reaction is pronounced. In the case of acetaldehyde, because of its low boiling point, much aldehyde is lost from the solution. Seyewetz and Bardin tried to overcome this difficulty by keeping the acetaldehyde content in their samples down to 7 to 8%. They also chilled the solutions to 4° to 5° C.

In attempts to use the Seyewetz and Bardin procedure, the above drawback was very evident. The equilibrium caused trouble with the low-boiling aldehyde because of consistent loss of aldehyde and with the higher boiling aldehydes because of the insolubility of the free aldehyde. The procedure can be used for determining formaldehyde (Seyewetz and Gibello, *8*) because of its relatively high solubility. A formaldehyde procedure of this type is described by D'Alelio (*2*).

Feinberg (*3*) found the sulfite method usable only in the case of formaldehyde and benzaldehyde, with not too reliable results in the case of benzaldehyde. He examined several neutral sulfite procedures and pointed out the difficulties in each, all due to equilibrium and end point. Feinberg suggested adding acid to the sulfite to make the reaction go to completion but made no quantitative study along these lines. He noticed how, when acid was added to aldehyde in sodium sulfite solutions, the pink phenolphthalein color disappeared and then gradually reappeared as more aldehyde reacted with sulfite. This showed the existence of a definite equilibrium.

Romeo and D'Amico (*6*), realizing the equilibrium difficulties in the previous procedures, used sodium sulfite–potassium bisulfite mixtures to determine cinnamaldehyde and benzaldehyde; they mentioned good results for cinnamaldehyde but poor results for benzaldehyde. They tried the method on some ketones, with generally poor results.

The function of the bisulfite would be to minimize the equilibrium which occurs when sulfite alone is used. However, because of the instability of bisulfite solutions, it was found advisable in the authors' work to use sulfuric acid instead. An aliquot of standard sulfuric acid is added to a large excess of sodium sulfite solution, so that sodium bisulfite is essentially the active ingredient. The acid is very stable and can stand for long periods of time without significant change in titer. It is added to the sulfite just before the aldehyde sample is introduced. The aldehyde reacts with the bisulfite, and the excess bisulfite is titrated with standard alkali. (The reaction might also be viewed as the aldehyde reacting with sulfite to liberate sodium hydroxide, and the acid present consuming the sodium hydroxide, pulling the reaction to completion.) The large excess of sulfite is to keep the reaction essentially at completion as the excess bisulfite is titrated with alkali. In this system, the reaction is so near completion that no aldehyde can be detected above the solution, even in the case of low-boiling aldehydes such as acetaldehyde. This reagent dissolves many insoluble, high-boiling aldehydes.

All the procedures mentioned above, using either neutral sulfite or sulfite-bisulfite, employed indicators for end point determination. This was unsatisfactory because the buffer systems involved dulled the end point. Adams and Adkins (*1*) tried color comparisons to minimize errors due to end point.

To detect the end point more accurately, it was found advisable to use a pH meter in the titration. A curve is plotted of pH *vs.* milliliters of standard alkali added, and the end point is determined from the curve. The end point in the case of each aldehyde comes at a rather definite pH (there is only slight deviation with the size of sample); once this pH is known, each sample can be titrated to it, thus eliminating the necessity of plotting a curve for each sample.

This procedure is rather generally applicable to determining aldehydes, and it has overcome the difficulties of equilibrium such as incomplete reaction, loss of sample, and poor titration, as well as the end-point difficulties encountered in the previous procedures, and has eliminated the necessity of using unstable standard solutions. This makes the procedure accurate, precise and very simple to operate, yet not lengthy.

APPARATUS

A 500-ml. glass-stoppered Erlenmeyer flask, a 600-ml. beaker, a pH meter, and standard electrodes.

Table I. Determination of Aldehydes

Aldehyde	pH Range of Solution at End Point	Observed Value, Mole	Mole of Sample Taken
Acetaldehyde	9.05–9.15	0.02455	0.02456
		0.02120	0.02118
		0.02858 (pH 9.1)[a]	0.02862
Propionaldehyde	9.30–9.50	0.02085	0.02090
		0.02037	0.02053
		0.01792 (pH 9.4)[a]	0.01811
Butyraldehyde	9.40–9.50	0.0249	0.0243
		0.0233	0.0236
		0.0275 (pH 9.45)[a]	0.0280
Cinnamaldehyde (takes on 2 moles of bisulfite per mole of sample)	9.50–9.60	0.0105	0.0106
		0.0108	0.0110
		0.0120 (pH 9.55)[a]	0.0122
Crotonaldehyde (takes on 2 moles of bisulfite per mole of sample)	9.20–9.40	0.0250	0.0253
		0.0189	0.0190
		0.0235 (pH 9.30)[a]	0.0238
Benzaldehyde	8.85–9.05	0.0163	0.0164
		0.0168	0.0173
		0.0147 (pH 8.95)[a]	0.0154

[a] Rapid method used.

All samples were distilled in a Podbielniak fractionating column (manufacturer claims 100 plates) and analyzed less than 2 hours after distillation to minimize air and autoxidation of sample.

SOLUTIONS

Sodium sulfite (1 *M*), standard 1 *N* sodium hydroxide, and standard 1 *N* sulfuric acid.

PROCEDURE

Fifty millimeters of 1 *N* sulfuric acid are added to 250 ml. of 1 *M* sodium sulfite in a 500-ml. glass-stoppered Erlenmeyer flask. To this solution is added a sample sealed in a glass ampoule containing 0.02 to 0.04 mole of aldehyde. The flask is stoppered, the stopper being greased in the case of low-boiling aldehydes to prevent any loss, then vigorously shaken to break the ampoule. Some glass beads included in the flask will cause the ampoule to break more easily. The flask is shaken for 2 to 3 minutes (5 minutes in the case of the more insoluble aldehydes) to ensure complete reaction. The contents are then quantitatively transferred to a beaker. Electrodes from a pH meter are inserted in the solution, and the solution is stirred. The pH of the solution is noted as standard 1 *N* alkali is added to titrate the excess acid.

For accurate results, the pH reading *vs.* milliliters of alkali added is noted and plotted. The end point is determined from the plot. A more rapid method of determining the end point, though slightly less precise, is to add alkali until a pH is obtained which corresponds to the pH at the end point for the particular aldehyde. This end-point pH can be taken from Table I or predetermined in cases of aldehydes not mentioned.

Sodium sulfite contains a small amount of free alkali as an impurity, so that 250 ml. of the solution consume some acid. The blank is very small but not negligible; it amounts to about 0.4 to 0.5 ml. of 1 *N* acid per 250 ml. of sulfite solution. On each carboy of sodium sulfite solution prepared, the free alkali should be accounted for or the aldehyde results will be slightly high. Rather than use a blank on the sulfite solution, it was found more satisfactory to add enough 1 *M* sodium bisulfite to the sodium sulfite to neutralize the free alkali and bring the pH of the sulfite to 9.1. This eliminates the blank and need be done only once to each carboy of solution.

DISCUSSION

In the case of most of the aldehydes used, the end point was sharp enough so that using the rapid method of simply titrating to the pH of the end point could cause an error in end-point determination of only ±0.2 to 0.3 ml. This error is not too significant and can be nullified by using a rather large sample of about 0.04 mole of aldehyde which consumes 40 ml. of 1 *N* acid. A plot of pH *vs.* milliliters of sodium hydroxide is not necessary once the pH at the end point of the particular aldehyde is determined. The reproducibility of the procedure is ±0.2% if the entire curve is plotted and ±0.4% if the rapid method is used.

The end point in the case of benzaldehyde is relatively poor (see Figure 1), and the rapid method could cause an error of ±0.4 to 0.5 ml. In this case a plot is necessary to determine the end point accurately.

Ketones cannot, on the whole, be determined by this method, even though they do form bisulfite addition products. Acetone, methyl ethyl ketone, quinone, naphthoquinone, and cyclohexanone were tried; cyclohexanone is the only ketone tried which might be determined by this method. The titration curves for ketones indicate that the ketone does react with bisulfite, but there is no discernible end point (see Figure 1). The pH climbs steadily on addition of the sodium hydroxide. In the case of cyclohexanone, a poor end point is obtained comparable to that of benzaldehyde. The titration curves in the case of ketones indicate that the equilibrium between ketone and ketone-bisulfite addition product leans toward free ketone and sodium bisulfite to a great extent. As sodium hydroxide is added, the pH rises gradually, but no break occurs in the curves. This can be explained by the consumption of excess sodium bisulfite by the sodium hydroxide, causing some ketone-bisulfite addition product to decompose, thus liberating some sodium bisulfite, so that the addition product is consumed along with the excess sodium bisulfite.

The explanation can be applied in the case of furfural, which behaves as do the ketones.

The poor end point in the case of benzaldehyde can be attributed to the same cause, but the equilibrium is enough in favor of the addition product to make this aldehyde determinable by this method.

Ketones, in general, will interfere in the determination of aldehydes only if they are present in excess of about 10 mole %. The aldehyde produces a break in the curve of pH *vs.* milliliters of sodium hydroxide, while the ketone does not. If ketones are present, the entire curve of pH *vs.* milliliters of sodium hydroxide has to be plotted and the break in the pH curve determined to obtain the end point, since, as indicated by Figure 1, the presence of ketones can affect the pH at the end point and, therefore, will cause erroneous results if the rapid method is used.

Acidic or basic impurities in the sample should be determined separately before the aldehyde procedure is applied, and the titration for the aldehyde should be corrected for their presence.

Acetals will not interfere in the procedure. These compounds hydrolyze in strong acid solution to yield acetaldehyde. However, the pH of the sodium sulfite–sulfuric acid solution, in proportions as described in the procedure, is about 6.8, and there is no noticeable hydrolysis of the acetals at this pH. The aldehyde in the sample consumes the bisulfite so rapidly that the pH of the solution is raised to about 7.5 as soon as the sample comes in contact with the sodium sulfite–sulfuric acid, further lessening any possibility of hydrolysis.

ACKNOWLEDGMENTS

The authors are indebted to L. T. Hallett, who proposed that an improved aldehyde procedure be developed, read the manu-

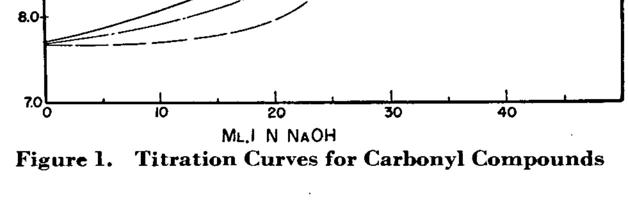


Figure 1. Titration Curves for Carbonyl Compounds

script, and made some valuable comments. They appreciate the assistance of John W. Copenhaver, who contributed valuable information that aided in the initiation of the problem.

The authors also wish to thank Richard S. Towne and Mrs. Fred Maisch, who purified and distilled the aldehydes used to test the procedure.

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Determination of Vinyl Ethers and Acetals

And of Any Alcohol, Acetaldehyde, and Water Contained Therein

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This procedure provides a means for quantitatively determining vinyl ethers and acetals and makes possible determination of acetaldehyde, alcohols, and water contained in the ether and acetal samples from the synthesis, or hydrolysis, of some of the vinyl ether or acetal. The acetals and vinyl ethers are determined by acid hydrolysis to acetaldehyde and determination of the acetaldehyde formed by the sodium sulfite–sulfuric acid method. No distillation of acetaldehyde is necessary. Where vinyl ether and acetal are present in the same sample, the sample is hydrolyzed and total acetaldehyde determined. Then the sample is hydrogenated to remove the vinyl ether as an interference, and this hydrogenated sample is hydrolyzed. This yields acetaldehyde from the acetal only. Subtracting this value from the total acetaldehyde yields acetaldehyde from the vinyl ether. Free acetaldehyde is determined by extracting the sample with sodium sulfite–sulfuric acid and titrating the excess acid. The vinyl ether and acetal values are corrected for free aldehyde in the sample. Acetylation of the samples and determination of acetic anhydride consumed yield the amount of alcohol present. Water is determined by the Karl Fischer reagent. For pure vinyl ethers and pure acetals the method yields results good to ±0.3%. When samples contain one or more of the components mentioned above, the errors have to be determined by accumulative error methods.

COMMERCIAL vinyl ethers may contain alcohol, acetaldehyde, water, and acetal. Alcohol may come from the original reactants in the synthesis of the ether or may be formed by hydrolysis of ether. Acetaldehyde originates by hydrolysis of the vinyl ether. Acetals are a product of a side reaction in the vinyl ether synthesis, and water enters the system in the washing process and sometimes with the alcohol.

The procedure developed for assaying vinyl ethers is also adaptable for assaying acetals. Since acetal syntheses involve alcohols, acetaldehydes, and water, as do the vinyl ethers, the procedures used to determine these impurities in vinyl ethers were applied and found to work as well in the case of acetals.

The scheme of analysis presented below makes possible the determination of acetaldehyde, alcohol, and water in the presence of either, or both, vinyl ether and acetal. It also makes possible the determination of vinyl ethers and acetals in the presence of both the above-mentioned impurities and of each other.

There has been very little done in the way of analytical procedures for vinyl ethers. Ruigh (*7*) attempted to determine divinyl ether in blood via hydrolysis to acetaldehyde. However, he encountered difficulty and had to resort to a more complicated method involving iodine pentoxide.

Attempts were made to determine vinyl ethers by quantitative hydrogenation, bromination, and titration with Karl Fischer's reagent. The hydrogenation method requires a long time to run an analysis and the reproducibility is poor. The reproducibility is poor also in the case of the Karl Fischer reagent. Bromination yielded no comprehensive results.

More work has been done in acetal determination than in the case of vinyl ethers. Many of the analytical methods are connected with measurement of hydrolysis rates of acetals and are unsuitable for absolute acetal determination, since the measurements are of a relative nature. They are perfectly adaptable for determining rate of hydrolysis but cannot readily be used to determine absolute amounts of acetal. Among such methods are those of Palomaa and Salonen (*4*) and of Tong and Olson (*11*), who followed the rate of hydrolysis of acetals via dilatometer measurements.

There have been methods for acetals where the acetal was hydrolyzed and the acetaldehyde determined. The drawbacks in these procedures are due, in most cases, to the shortcomings of the acetaldehyde procedure used (*9*). Many of the procedures distill the acetaldehyde over into the medium in which it is to be determined. This step not only greatly increases the time required for an analysis but also can be a source of error. Peynaud (*5*) determined acetal by distilling acetaldehyde over into a potassium dihydrogen phosphate–disodium phosphate buffer containing sodium bisulfite and determined aldehyde by the iodometric measurement of excess bisulfite. This method has the disadvantage of the distillation, and the iodometric bisulfite method for aldehyde determination also has shortcomings (*9*).

Orton and McKie (*3*) hydrolyzed and distilled acetaldehyde into sodium bisulfite using the Ripper (*6*) method for determining excess bisulfite iodometrically. They also used the Seyewetz and Bardin procedure (*8*) which determines increase in alkalinity of a sodium sulfite solution as acetaldehyde. Here again the distillation and weaknesses of the acetaldehyde procedures (*9*) limit the desirability of using this procedure.

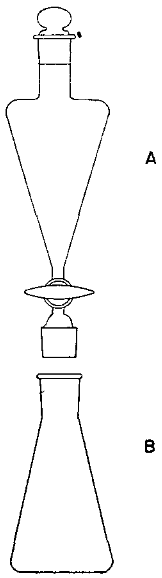

Figure 1. Apparatus for Determination of Vinyl Ethers and Acetal

Hähnel and Lennerstrand (*1*) avoided the distillation and used a hydroxylamine method to determine acetaldehyde. The end points are admittedly bad, and dilutions to volume and color comparisons are necessary to obtain the end point. They also used iodometric-bisulfite procedures but realized the instability of the solution and the need for daily standardization.

The procedure for determining vinyl ethers and acetals as described below requires only 30 minutes to run. Since all the reactions are run in the same closed vessel, there is less danger of loss by volatilization of acetaldehyde. The reagents used are stable, and there are no end-point or equilibrium difficulties to harass the operator. There is no need for distilling the acetaldehyde to determine it; the acetaldehyde is determined in the hydrolysis reaction mixture. The procedure is accurate and precise to ±0.3%.

The alcohol procedure used is that described by Ogg, Porter, and Willits (*2*). A pretreatment (hydrogenation) of the sample is necessary in the case of the vinyl ethers, where water is also present, before the alcohol procedure can be applied. No pretreatment is necessary for determining alcohols in acetals.

Hydrogenation of the sample is also necessary in the case of water determination. The procedure used is that described by Smith, Bryant, and Mitchell (*10*), employing Karl Fischer's reagent.

APPARATUS

For vinyl ether and acetal determination, the apparatus is as shown in Figure 1. The top portion, *A*, consists of a 500-ml. Erlenmeyer flask with a 29/26 standard-taper ground-glass female joint blown onto the bottom with glass stoppers to fit. To the mouth of the flask is attached a 6-mm. stopcock, and onto the stopcock is put a 29/26 standard-taper ground-glass male joint.

The bottom portion of the apparatus, *B*, is a 500-ml. Erlenmeyer flask with a 29/26 standard-taper female joint sealed onto the mouth. In determining the acetaldehyde, only the bottom portion of the apparatus is necessary.

Alcohol determination requires 150- to 200-ml. Pyrex short-necked Florence flasks equipped with ground joints to fit condensers. This enables the sample to be refluxed with the reagents and permits titration in the reaction flask without transfer.

The hydrogenation apparatus is of simple construction (Figure 2). The hydrogenation vessel consists of a 250-ml. wash bottle equipped with ground joints for use with organic liquids. To its exit arm is attached a 2-way stopcock. The blowing arm is cut short, and a ground-glass female joint is attached to accommodate the 25.4-cm. (10-inch) condenser. The bubble tower is used to control pressure during the hydrogenation. The height of mercury in the tower keeps the pressure in the apparatus constant as excess hydrogen bubbles through the mercury. Increased pressure increases speed of hydrogenation. However, too much pressure is undesirable, since it opens the ground-glass joints.

The apparatus can be modified to enable hydrogenation of four samples at one time, by lengthening the tube from the pressure control tower to the reaction section. Four separate reaction sections can then be led off this tube, all controlled by the same pressure. A stopcock between the condenser of each reaction section and the manifold should be included, so that the system can be used for less than four hydrogenations if necessary.

From 25 to 30 cm. of mercury were found suitable for rapid hydrogenation without causing the glass joints to open.

A magnetic stirrer is used for agitation. A magnet attached to the shaft of a stirring motor acting on an iron paddle in the hydrogenation vessel provided agitation during the hydrogenation.

In the water determination, an automatic refilling buret is desirable, so that the Karl Fischer reagent has minimum contact with air.

REAGENTS

Vinyl Ether, Acetals, and Acetaldehyde require standard 1 *N* sulfuric acid, standard 1 *N* sodium hydroxide, and 1 *M* sodium sulfite.

Alcohol requires a solution of 1 part of c.p. acetic anhydride to 3 parts of c.p. pyridine as the acetylating mixture. This solution should be prepared fresh each day. The indicator used in this analysis is a mixture of 1 part of 0.1% cresol red and 3 parts of 0.1% thymol blue (a few drops of sodium hydroxide solution are necessary to get dyes into solution). c.p. *n*-butyl alcohol is used as a wash liquid.

Water. The Karl Fischer reagent used is as prepared by Smith, Bryant, and Mitchell (*10*)—84.7 grams of iodine in a mixture of 269 ml. of c.p. pyridine and 667 ml. of c.p. methanol. The solution is cooled in ice water, and 64 grams of sulfur dioxide are added.

PROCEDURE

A. Acetaldehyde. A measured sample (which should be hydrogenated if vinyl ether is present) containing not more than 0.01 mole of acetaldehyde, is introduced into a 500-ml. glass-stoppered Erlenmeyer flask containing 250 ml. of 1 *M* sodium sulfite solution and 10 ml. of standard 1 *N* sulfuric acid. The pH of the sodium sulfite–sulfuric acid solution is about 8.0, and no significant amount of acetal is hydrolyzed at this pH. The mixture is vigorously shaken for 15 minutes to ensure extraction of all the acetaldehyde from the sample. The contents of the flask are then quantitatively transferred to a 600-ml. beaker. Electrodes from a pH meter are inserted in the solution, and the solution, while being mechanically stirred, is titrated with standard 1 *N* sodium hydroxide.

For accurate results, a curve is plotted of pH *vs.* milliliters of sodium hydroxide added, and the end point is determined exactly (*9*). For more rapid though slightly less accurate work the solution can be titrated to a definite pH (pH at the end point as determined by experiment). The end point can be taken at pH 9.1 for acetaldehyde.

The sodium sulfite contains some free alkali which will cause high results unless neutralized with sodium bisulfite (*9*).

A qualitative test, the standard Tollens test for aldehydes, can be made on the sample. If negative, a quantitative aldehyde analysis is unnecessary. Samples containing vinyl ether do not have to be hydrogenated for this test. If a silver mirror forms,

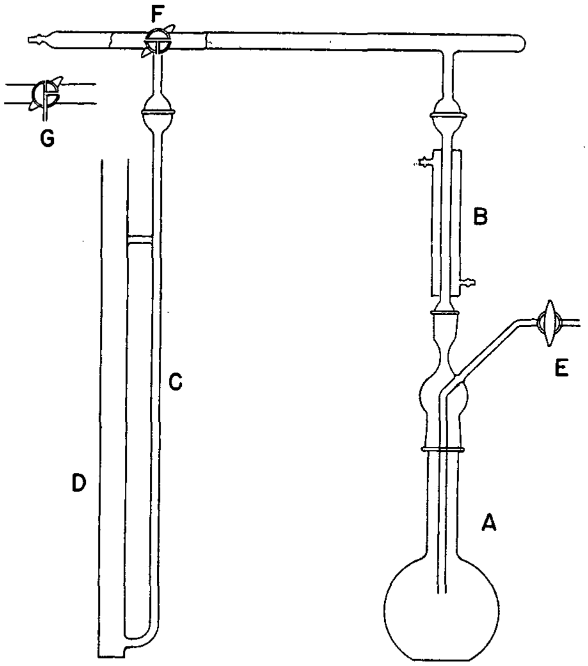

Figure 2. Hydrogenation Apparatus

enough aldehyde is present to be determined quantitatively. However, if no mirror is formed after the shaking, or if only a very slight mirror is formed on the flask at the liquid surface, the amount of aldehyde present is too small to be determined quantitatively.

B. Vinyl Ethers and Acetals. A sample of 0.02 to 0.04 mole of ether or acetal is weighed in a sealed thin-walled ampoule and is introduced into section *A* of the apparatus shown in Figure 1 along with 50 ml. of standard 1 *N* sulfuric acid. Glass beads are included to aid in breaking the ampoule. The apparatus is stoppered, the stopper being well greased to prevent any leakage of acetaldehyde, and is totally immersed in an ice-water mixture for 5 minutes. The chilling is to create a decreased pressure in the flask by contracting the air above the liquid. The temperature of the solutions in the flask will drop to 10° to 15° C., about 8° below the boiling point of acetaldehyde. When the ampoule is broken, there will not be too great a pressure in the flask; if the flask is not chilled, the stoppers sometimes are forced open. In the case of methyl vinyl ether (boiling point 5-6° C.), the flask should be chilled thoroughly (20 minutes). The low boiling point of this ether causes the stoppers to blow as soon as the ampoule is broken. The stopper should be held firmly until the ether is hydrolyzed to prevent blowing out.

After the flask is chilled, it is vigorously shaken to break the ampoule containing the sample, then for 15 minutes more to ensure complete hydrolysis of the sample.

For most acetals and vinyl ethers, 15 minutes' shaking is sufficient, but for some—for example, di-*n*-butyl acetal—30 minutes are necessary to ensure complete hydrolysis. A Kahn shaker was used, in which the stopper is clamped on the flask while shaking is in progress.

After hydrolysis is complete, *A*, containing the hydrolyzed sample, is attached to *B*, which contains 250 ml. of 1 *M* sodium sulfite. The joint connecting the two sections should be greased to prevent loss of acetaldehyde. Then the stopcock in *A* is opened, and the acid solution containing the aldehyde is shaken down into the sulfite solution. The acid and sulfite form bisulfite which consumes the acetaldehyde. After all the acid solution is down in *B*, some of the solution from *B* is shaken back into *A* to react with the acetaldehyde contained on the walls and on the glass beads. The whole apparatus is vigorously shaken for a few minutes to assure removal of all acetaldehyde from the atmosphere in both sections of the apparatus.

The sections of the apparatus are then separated and rinsed quantitatively into an 800- or 1000-ml. beaker, and the solution is titrated with standard 1 *N* sodium hydroxide, using a pH meter as in the acetaldehyde determination. Plotting pH *vs.* milliliters of sodium hydroxide is the most accurate method of determining the end point. However, this titration is large, and titrating to pH 9.1 incurs no very significant error.

Any free aldehyde in the sample is determined and the value subtracted from the figures for vinyl ether or acetal.

If the sample contains aldehyde, vinyl ether, and acetal, the above procedure will yield a combined value for all three. The free aldehyde is determined separately, as described, and subtracted from the total aldehyde. The difference is the combined acetaldehyde from both the vinyl ether and the acetal. The procedure is repeated on a hydrogenated sample where the vinyl ether in the sample is saturated and no longer yields any acetaldehyde. The procedure on the hydrogenated sample will yield the acetaldehyde from the acetal (the free aldehyde is also picked up, and the acetal figure has to be corrected for the free aldehyde). The cases where acetaldehyde, vinyl ether, and acetal occur together can be summarized as follows:

1. Procedure A on the hydrogenated sample yields free acetaldehyde on the sample.
2. Procedure B on the sample yields free acetaldehyde plus acetaldehyde from the vinyl ether plus acetaldehyde from the acetal.
3. Procedure B on the hydrogenated sample yields free acetaldehyde plus acetaldehyde from the acetal.

Therefore, (1) yields free acetaldehyde; (3) minus (1) yields acetal; and (3) minus (2) yields vinyl ether.

C. Hydrogenation. About 20 ml. of sample are put in the hydrogenation vessel, *A* (Figure 2) along with about 1 gram of Adam's catalyst (the same catalyst can be used for five to ten hydrogenations), and the iron paddle used for stirring. All joints are greased and clamped closed to hold the pressure of about 25 cm. of mercury in the pressure control tower, *D*. The reaction flask is chilled in a dry ice–methanol mixture to avoid loss while the system is being flushed with hydrogen. The apparatus is then flushed with a slow stream of hydrogen for 2 to 3 minutes. The exit stopcock, *E*, on the flask is closed, the dry ice–methanol is removed, and the magnetic stirrer under the flask is turned on, to rotate the iron paddle in the flask. The more vigorous the stirring, the faster the hydrogenation will go.

The hydrogen rate should not be too fast, since it will cause vapors to be blown out of the system and thus cause varying composition of the sample. Yet enough hydrogen should be used so that excess can be noted bubbling through the mercury in the pressure control tower. One bubble of hydrogen per second is perfectly safe for all samples if the acetaldehyde content is not greater than 3%. If the sample contains over 5% acetaldehyde, the condenser should be cooled by circulating ice water through the jacket.

The flask becomes warm as hydrogenation begins (the purpose of condenser *B* is to catch any vapors) and gradually cools down as hydrogenation comes to completion. Hydrogenation is usually complete when the flask is cool to the touch; however, the reaction mixture can, and should, be tested. Stopcock *F* is turned to the position shown in *G* of Figure 2. If the sample is not completely hydrogenated, it will continue to consume the hydrogen contained in the apparatus, and the mercury will be seen rising in capillary tube *C*. If this is the case, *F* is turned to its former position and hydrogenation is continued (agitation is continued throughout the testing). If the mercury does not rise, the sample is completely hydrogenated. The sample is chilled with ice water, and the condenser is rinsed with some liquid from the flask to keep composition of the sample constant. The ether is transferred while cold to a centrifuge tube equipped with a soft cork stopper. The catalyst is then centrifuged off, and samples of the supernatant liquid are drawn up and sealed in ampoules.

The time required for the hydrogenation process varies with the condition of the catalyst. For 20 ml. of vinyl ether and 1 gram of catalyst, the hydrogenation will take 1 to 2 hours if the catalyst is fresh and as yet unused. The rate of hydrogenation increases with the use of catalyst; after about three hydrogenations, the catalyst will cause the next hydrogenation to be complete in about 30 minutes. If the catalyst is used for more than ten hydrogenations the reaction goes with such vigor that much heat is generated in the hydrogenation flask, and some vapor may get past the condenser, causing loss of sample and disrupting the composition of the mixture.

In samples of methyl vinyl ether it is not necessary to hydrogenate all the methyl vinyl ether. The purpose of the hydrogenation is to inactivate the ether, but most of the methyl vinyl ether can be eliminated by allowing it to volatilize. However, when this is done it is necessary to weigh the sample before hydrogenation. If the sample contains more than 5% acetaldehyde, it is best to hydrogenate the entire sample of methyl vinyl ether to prevent loss of aldehyde.

A sample of methyl vinyl ether is weighed in a sealed glass ampoule and put in the hydrogenation vessel with about 30 ml. of di-*n*-butyl ether. The flask is chilled in dry ice–methanol and the ampoule is broken with a glass rod, which is rinsed with dibutyl ether. The flask is allowed to come to room temperature and the methyl vinyl ether is allowed to escape. Some Adam's catalyst is then added to the flask and any methyl vinyl ether remaining in solution is hydrogenated as described above.

CAUTION. There are precautions to be observed in use of the catalyst as well as in the handling of hydrogen. Adam's catalyst (platinum oxide) when dry will become hot and will glow in a stream of hydrogen when oxygen is present. Therefore, on beginning the hydrogenation it is well to shake the flask and make sure all particles of catalyst are wet with sample and the apparatus should be flushed sufficiently to remove all oxygen. When wet, the catalyst does not heat up and gets warm only after the hydrogenation is under way. A glowing particle of catalyst can ignite the hydrogen-air-vapor mixture at the commencement of the hydrogenation and cause it to flash, if not explode.

D. Alcohol. A measured sample, containing about 4 to 7 milliequivalents of alcohol, is put in a 150 to 200-ml. short-necked Florence flask with ground joint to fit the condenser. The sample should be hydrogenated if it contains vinyl ether in the presence of water. If the sample is absolutely dry, the procedure can be applied to vinyl ethers without hydrogenation. Water in the samples causes some hydrolysis of the ether when the sample hits the acetic anhydride before the anhydride can consume all the water; this causes high results. To the sample are added 5 ml. of acetic anhydride in pyridine (1 part of anhydride to 3 parts of pyridine). The mixture is heated under reflux on a steam bath for 45 to 60 minutes, the ground joint being kept wet with pyridine. Then 5 to 6 ml. of water are added through the condenser and the mixture is heated further for 2 to 3 minutes. The condenser is rinsed into the flask with C.P. *n*-butanol, and the contents of the flask are titrated with standard 0.5 *N* alcoholic sodium hydroxide, using a few drops of mixed indicator (1 part of 0.1% cresol red and 3 parts of 0.1% thymol blue with a few drops of dilute sodium hydroxide added to dissolve the dyes). A blank is run on 5 ml. of the anhydride reagent.

If the sample contains acetaldehyde, phthalic anhydride should be used instead of acetic anhydride. Acetaldehyde consumes some acetic anhydride, to cause slightly high results. Fifty milliliters of 1 *M* phthalic anhydride are added, and the procedure is carried out identically as with the acetic anhydride except that 1 *M* sodium hydroxide is used in the final titration with phenolphthalein indicator.

E. Water (*10*). A measured sample (which has been hydrogenated if it contains vinyl ether) is titrated with Karl Fischer's reagent to a permanent iodine coloration. If the sample is small, it is dissolved in methanol or pyridine on which a blank titration has been run.

Directions for preparation, standardization, and storage of Karl Fischer reagent are given in (*10*).

A quick test to determine the presence of water is to chill the sample in dry ice–methanol. If the sample remains clear, or if only a turbidity develops, the water content is 0.2% or less. If particles of ice are detected, a quantitative water test should be run.

Samples from the actual synthesis of vinyl ethers were analyzed by the above methods and were distilled in a Podbielniak distilling apparatus (manufacturer claims 100 plates). The distillation results, obtained by taking the weight of each fraction and dividing by the total sample distilled, compared very favorably with the chemical analysis.

DISCUSSION

Acetal samples, where there is no vinyl ether present, are simpler to handle than the samples containing vinyl ether, since no hydrogenation is required to determine aldehyde, alcohol, water, and acetal. All analyses are run on the sample itself.

In hydrogenating vinyl ether–containing samples, it is important not to bubble hydrogen through the apparatus so fast that loss of sample will take place. The temperature of the water in the condenser should be below 15° C. to make sure of catching any acetaldehyde. Samples of ether have been analyzed containing up to 5% acetaldehyde, and no loss of aldehyde is noticed on hydrogenation.

Aldehyde is best run on a hydrogenated sample if vinyl ethers are present. Apparently the ether ties up some bisulfite in an equilibrium reaction. This equilibrium slows the end point and can give very erroneous results if the sample is titrated too fast. In unhydrogenated samples, it is necessary, on approaching the end point, to wait a few minutes after each addition of sodium hydroxide until the equilibrium readjusts itself. In this way, the bisulfite tied up by the ether can be accounted for. This procedure is lengthy and can cause serious error. On samples containing hydrogenated vinyl ether, or on acetal samples, the procedure is fast, the end point sharp, and there is much less chance for error.

Similar results were obtained in the alcohol determination. Acetic anhydride does not react with vinyl ethers if the ether is absolutely dry. A small percentage of the vinyl ether present is hydrolyzed by the water contained in the sample in the presence of the acidic reagents used to form some alcohol. The anhydride does not consume the water fast enough to prevent the hydrolysis of the ether. This small amount is usually very significant, since the alcohol content of most of these samples is small. However, hydrogenated vinyl ether samples and acetal samples give no trouble.

In determining water in vinyl ether samples, hydrogenation is very necessary, since Karl Fischer's reagent reacts readily with vinyl ether. The nature of the reaction between the reagent and the ether is not known, but is rather rapid.

In the determination of vinyl ethers and acetals, the time of hydrolysis depends on vigor of shaking and ease of hydrolysis of the particular ether or acetal. The shaking is important since the samples are immiscible with water, and the more vigorous the shaking, the more sample surface is in contact with acid. The procedure as described calls for 15 minutes' rather leisurely shaking for complete hydrolysis. The hydrolysis can be completed in 5 minutes of vigorous shaking if the sample is well mixed with the acid. If the shaking is too leisurely or the flask is not shaken at all, the hydrolysis may not be complete even after 15 minutes.

The nature of the sample has a great deal to do with the hydrolysis. Methyl vinyl ether hydrolyzes very readily and will be complete in 5 minutes with easy shaking of acid and sample. *n*-Butyl vinyl ether hydrolyzes much less readily, and the full 15 minutes of shaking with the acid are required, unless the shaking is very vigorous. In the case of the acetals, the same is true. Dimethyl acetal hydrolyzes very easily. However, di-*n*-butyl acetal requires more vigorous treatment than even the *n*-butyl vinyl ether. To ensure complete hydrolysis, this acetal should be shaken vigorously with the acid for 15 minutes, or for 30 minutes, if agitation is moderate.

The dropping of the hydrolysis reaction mixture into the sulfite solution and titration of the resultant solution eliminates the time-consuming distillation of acetaldehyde used in former acetal procedures. The sodium sulfite–sulfuric acid procedure for acetaldehyde is preferable to previous aldehyde procedures (*9*). The fact that the hydrolysis and reaction of the acetaldehyde with the sulfite–sulfuric acid are all carried out in one closed system eliminates the danger of error due to loss of acet-

Table I. Results on Pure[a] Vinyl Ethers and Acetals

	Observed, Mole	Mole of Sample Taken
Methyl vinyl ether	0.04212 0.04227 (at pH 9.1)[b]	0.04235
	0.03216 0.03216 (at pH 9.1)	0.03237
Ethyl vinyl ether	0.04241 0.04241 (at pH 9.1)	0.4244
	0.03743 0.03757 (at pH 9.1)	0.03742
	0.02683	0.02683
Isopropyl vinyl ether	0.03515 0.03515 (at pH 9.1)	0.03516
	0.04070 0.04056 (at pH 9.1)	0.04079
n-Butyl vinyl ether	0.05378	0.05381
	0.04988	0.05007
	0.05183	0.05189
	0.04447	0.04457
Isobutyl vinyl ether	0.02461	0.02468
	0.01407	0.01405
	0.02273	0.02267
Dimethyl acetal	0.02565	0.02575
	0.03672	0.03679
Diisopropyl acetal	0.03625	0.03674
	0.03633	0.03674
Di-*n*-butyl acetal	0.00660	0.00662
	0.00932	0.00939

[a] All samples were thoroughly washed, dried, and twice distilled in a 30-plate column over KOH or sodium to ensure purity.
[b] Result if end point were taken at pH 9.1.

Table II. Acetaldehyde in Presence of Vinyl Ether and Acetal

Acetaldehyde Sample, Mole	Added	Acetaldehyde Found, Mole
0.00195	10 ml. *n*-butyl vinyl ether	0.00195
0.00195	10 ml. di-*n*-butyl acetal	0.00194

Table III. Diisopropyl Acetal and Isopropyl Vinyl Ether in Presence of Each Other

(50-50% by weight mixture)

% Acetal Found	% Ether Found
50.2	49.9
49.5	49.2

Table IV. Alcohol in Presence of Hydrogenated *n*-Butyl Vinyl Ether

(0.00168 mole of butanol + 10 ml. of hydrogenated *n*-butyl vinyl ether)

Alcohol Found

1. Butanol, 0.00164 mole
2. Butanol, 0.00159 mole
3. Butanol, 0.00160 mole

Table V. Prepared Mixture of Known Amounts of Acetaldehyde, *n*-Butyl Vinyl Ether, Di-*n*-butyl Acetal, Butanol, and Water

	Theoretical %	Found %
Acetaldehyde	1.48	1.32
n-Butyl vinyl ether	44.43	44.8
Dibutyl acetal	49.01	49.9
Butanol	4.78	4.7
H_2O	0.30	0.24

aldehyde. These factors lend a high accuracy and precision to the procedure, and the time required for an analysis is only about 30 minutes (45 to 60 minutes if the end point is determined by plotting the curve of pH *vs.* milliliters of sodium hydroxide). Using two sets of apparatus simultaneously and titrating to a predetermined pH value, a technician can run four determinations per hour, including sealing samples in ampoules and weighing.

The ability to determine alcohol, acetaldehyde, and water in the vinyl ether and acetal samples is important in following the synthesis or hydrolytic decomposition of acetals and vinyl ethers, since these compounds are involved in these chemical processes. The ability to determine acetal and vinyl ether in the presence of each other is important, since acetals are sometimes formed in vinyl ether synthesis.

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Method for Isolation of Hemicelluloses Directly from Maple Wood

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A method for the extraction of hemicelluloses from maple wood is more rapid and produces higher yields of hemicelluloses than previous methods. Wood sawdust, 20- to 40-mesh, is treated with 20% potassium hydroxide at 65° to 70° C. for 2 hours. Water is added to reduce the potassium hydroxide to 3% concentration, in which the sawdust is treated for 2 more hours at 65° to 70° C. The hemicelluloses in the alkaline solution are then filtered and pressed from the residual sawdust, precipitated from the alkaline solution by addition of methyl alcohol, and bleached with sodium chlorite to remove traces of lignin. They contained 75 to 80% of pentosans, considerable uronic acids, and some methoxyl groups. The wood residue after removal of the hemicelluloses still contained appreciable percentages of these materials. It was partially delignified with sodium chlorite, then treated at 65° to 70° C. for 2 hours with 20% potassium hydroxide solution, which was diluted with water to 3.0% concentration, and the treatment was continued for 2 hours more, as was done to the original sawdust. The alkaline treatment removed 12.5% of material, but only 3.5% was recovered as hemicelluloses.

ALTHOUGH several methods have been used for the isolation of hemicelluloses from wood, it is still highly desirable to develop procedures for increasing the yield of these materials and reducing the time of operation.

Hemicelluloses as discussed in this article are the materials in wood holocellulose (hemicelluloses plus α-cellulose) that are soluble in 17.5% sodium hydroxide solution under the conditions specified for the determination of α-cellulose (*5*).

Hemicelluloses have been isolated from wood and holocellulose by a number of methods with varying results.

Wheeler and Tollens (*12*), by one extraction with cold 5.0 to 10.0% sodium hydroxide solution, obtained from birch wood 4.0 to 5.0% of a material that they called wood gum. O'Dwyer (*8*), with 4.0% sodium hydroxide solution, isolated approximately 5.0% of hemicelluloses from beech wood. Sands and Nutter (*10*) extracted mesquite sawdust with 5.0% sodium hydroxide solution, then chlorinated the wood residue, and extracted the chlorinated residue with cold 10.0% sodium hydroxide solution for 24 hours. They reported yields of approximately 7.0% hemicelluloses. The yields of materials extracted directly from wood by these methods are all low.

Anderson and co-workers (*1, 2, 3*) reported several yields of hemicelluloses from woods. They extracted the wood at room temperature with 5.0% aqueous sodium hydroxide twice, each time for 48 hours, chlorinated it, and again extracted it twice with 5.0% aqueous sodium hydroxide for 48 hours at room temperature. This series of treatments of 192 hours produced an accumulative yield of approximately 14.0% of hemicelluloses, with no correction for lignin or ash, from white birch, lemon, and black locust. Preece (*9*), in some careful work, extracted teak wood with 4.0% sodium hydroxide for different periods and at different temperatures in order to determine the effect of these factors on the furfural yield from the treated wood as compared with that from the untreated wood. Boiling temperatures of the alkali caused losses in the yield of furfural from the hemicellulose. Alternately dissolving and reprecipitating the hemicelluloses during purification degraded the materials.

Kurth and Ritter (*6*), by means of 1.0% sulfuric acid, removed 14.5% of the hemicelluloses from spruce holocellulose that had been prepared by chlorinating and then extracting the chlorinated wood with an alcohol-pyridine mixture for dissolving the chlorinated lignin. Wise, Murphy, and D'Addieco (*14*) used sodium chlorite to prepare holocellulose from which 20.0% of hemicelluloses were removed by two extractions with potassium hydroxide. Thomas (*11*) prepared hemicelluloses from aspen holocelluoses by a series of extractions with cold water, hot water, and two different concentrations of potassium hydroxide. He obtained good yields of the materials and determined the composition of the various fractions. As in the two preceding researches, his approach first required the preparation of holocellulose, which increased the time of operation.

In order to facilitate the isolation of increased quantities of hemicelluloses for intensive fundamental research, work was begun at the Forest Products Laboratory on developing a method for extracting the hemicelluloses directly from wood sawdust. Previous workers (*8, 10, 12*) had shown that, if the yields of hemicelluloses from such extractions were to be substantially increased, it would be necessary to treat the wood so as to loosen the hemicelluloses more thoroughly from the other wood components.

FEATURES OF METHOD

Preliminary experiments with 2-gram samples of air-dry sugar maple sawdust, 20- to 40-mesh, showed that by using a two-step alkaline extraction at elevated temperatures, the yield of hemicelluloses could be substantially increased.

The first step was to treat the sugar maple sawdust with strong hydroxide solution for 1 to 2 hours at 65° to 70° C. The next was to add sufficient water to the alkali to reduce it to a concentration of 3% in the solution, in which the sawdust was allowed to remain for 2 more hours at 65° to 70° C. During both treatments, the sawdust was stirred frequently, so that the concentration of the alkali and the temperature would remain uniform throughout the mixture. After 2 hours in the dilute alkali, the dissolved hemicelluloses were filtered or pressed out of the sawdust. Two volumes of absolute (commercial grade) methyl alcohol were poured into the alkaline filtrate to precipitate the hemicelluloses.

On the basis of data gathered in the preliminary experiments on 2-, 100-, and 200-gram samples, the following procedure was developed for preparing hemicelluloses from 500-gram samples of sugar maple sawdust. The composition of the original maple wood was as follows:

	%
Extractives	
Hot water	3.90
Ether	0.30
Ash	0.24
Holocellulose	74.50
Lignin	21.60
	100.54
α-Cellulose	50.00
Acetyl	3.60
Methoxyl	6.90
Uronic acid anhydride	4.36

The composition of the maple hemicelluloses is given in Tables I and II.

PROCEDURE

Place 525 grams of air-dry (500 grams, oven-dry) sugar maple sawdust, 20- to 40-mesh, in a 10-quart stainless-steel bucket, add 884 ml. of 20% aqueous potassium hydroxide solution, and mix thoroughly to ensure intimate contact between the alkali and the wood. Place the bucket and contents in a water bath at 67° C. for 2 hours; stir the mixture frequently during this period.

After 2 hours' treatment in the strong alkali, add 5900 ml. of distilled water to the mixture so as to reduce the alkali concentration to 3%. Carry out the treatment at 67° C. in the 3% alkali with constant stirring of the alkali-wood mixture for 2 hours.

Place the alkali-wood mixture in canvas bags and subject it to a hand press to remove the alkaline filtrate containing hemicelluloses. Transfer the wood residue to a Büchner funnel, wash three times with hot water, and press the residual sawdust cake with a spatula in order to remove adhering hemicelluloses. Add the washings to the initial filtrate of hemicelluloses.

Then wash the extracted wood residue with water acidified with acetic acid to remove ash-forming chemicals. Dry and weigh the residue for subsequent use.

Precipitate the hemicelluloses from the alkaline filtrate by adding two volumes of absolute methyl alcohol. Allow the mixture to stand so that the hemicelluloses will settle. Siphon off the supernatant liquid and transfer the residual mixture to a Büchner funnel for filtering and pressing with a spatula.

Transfer the hemicelluloses to a beaker for bleaching with sodium chlorite, so as to remove traces of lignin. Bleaching is carried out by adding a mixture consisting of 1.5 liters of methyl alcohol and 100 ml. of water made faintly acid to litmus with acetic acid. Raise the temperature to 65° to 70° C. and slowly add a concentrated solution of aqueous sodium chlorite dropwise until the odor of chlorine dioxide is detected. Continue the bleaching until the hemicelluloses appear greenish white in the bleach solution. Transfer the bleached material to a Büchner funnel; filter and press it with a spatula to remove as much filtrate as possible.

Purify the bleached hemicelluloses by redissolving them in a small volume of dilute aqueous potassium hydroxide solution in a beaker. Then reprecipitate them with three volumes of methyl alcohol containing sufficient acetic acid for neutralizing the potassium hydroxide in the solution (they settle quickly and thus enable siphoning off of the supernatant alcohol, which removes residual potassium acetate from the bleached material). Con-

Table I. Yield and Percentage Composition of Materials

Material	Operation	Yield on Basis of Original Wood %	Ash %	Lignin %	Methoxyl %	Pentosan %	Uronic Acid Anhydride %
Sugar maple wood[a]		100.0	0.24	21.62	6.36	23.90	4.36
Hemicelluloses-1[b]	Sugar-maple wood to hemicelluloses-1	14.6	7.10	0	2.15	76.60	16.67
Wood residue[b]	Sugar-maple wood to wood residue from alkaline extraction	71.2	8.60	26.55	7.13	11.45	2.42
Partially delignified wood residue[b]	Wood residue to partially delignified wood residue	52.5	0.37	4.70	2.18	11.50	2.55
Hemicelluloses-2[b]	Partially delignified wood residue to hemicelluloses-2	3.5	7.16	5.20	3.03	77.70	9.80
Cellulose residue[b]	Partially delignified wood residue minus second alkaline extraction	40.0	0.17	0.72	0.48	5.25	1.51

[a] Values for wood calculated on weight of oven-dry material.
[b] Values for wood fractions calculated on weight of oven-dry ash-free material.

Table II. Yield and Composition of Maple Wood and Its Fractions

	Yield Data				Composition Data			
Material	Used in Preparation %	Removed %	Recovered %	Lost %	Lignin %	Methoxyl %	Pentosan %	Uronic acid anhydride %
Maple wood[a]	...	...	...	...	21.62	6.36	23.90	4.36
Hemicelluloses-1[b]	100.0	28.8	14.6	14.2	0	0.31	11.19	2.43
Wood residue[b]	...	...	71.2	...	18.90	5.12	8.20	1.73
Partially delignified wood residue[b]	71.2	18.7	52.5	...	2.47	1.14	6.04	1.36
Hemicelluloses-2[b]	52.5	12.5	3.5	9.0	0.18	0.10	2.64	0.33
Cellulose residue[b]	...	...	40.0	...	0.29	0.19	2.10	0.60

[a] Values for wood calculated on weight of oven-dry material.

[b] Values for yields and oven-dry ash-free wood fractions calculated on weight of oven-dry wood.

tinue the purification of the hemicelluloses by adding methyl alcohol, allowing it to stand 15 minutes, and siphoning off the supernatant liquid. Repeat this last operation three times, and finally transfer the mixture to a Büchner funnel for removing excess alcohol by filtering and pressing with a spatula to improve the texture of the material, which at this stage is a white, porous, crumbly mass. Then suspend this residue in 1 liter of anhydrous acetone for 2 hours; filter and press it, and then transfer it to a crystallizing dish for removing the excess liquid.

Remove the residual acetone slowly, so as to avoid rapid cooling and condensation of moisture on the hemicelluloses. To do this, place the crystallizing dish and contents in a desiccator evacuated at room temperature by a water suction pump for 24 hours. During drying, turn the material with a spatula several times. Finally heat the dish with contents at 70° C. in a steam oven until dry.

The yield of hemicelluloses on an ash-free, lignin-free basis from sugar maple by this procedure, in the work performed at the Forest Products Laboratory, was approximately 14.6% of the weight of the oven-dry wood. The material so obtained was designated as hemicelluloses-1.

HEMICELLULOSES IN WOOD RESIDUE

Some hemicelluloses were retained in the wood residue remaining after hemicelluloses-1 had been extracted from the wood. They appeared to be too closely associated with other wood components in the residue to be removed during the isolation of hemicelluloses-1. In attempting to render them more soluble, the wood residue was partially delignified by treatment with sodium chlorite as reported by Wise, Murphy, and D'Addieco (*14*) for the preparation of holocellulose. The partially delignified residue was then subjected to the procedure for preparing hemicelluloses-1. The materials so recovered were designated as hemicelluloses-2.

COMPOSITION OF VARIOUS WOOD FRACTIONS

Isolation of hemicelluloses-1 and -2 involved separation of the following wood fractions: (1) unprocessed wood, (2) hemicelluloses-1, (3) wood residue, (4) partially delignified wood residue, (5) hemicelluloses-2, and (6) cellulose residue.

These wood fractions were analyzed in order to trace the progress in removing their components. The analytical data are recorded in Table I.

Moisture, ash, lignin, pentosans, and holocellulose were determined by Forest Products Laboratory methods (*5*), methoxyl according to Clark (*4*), and uronic acids according to Whistler, Martin, and Harris (*13*).

Ash. Percentages of ash in hemicelluloses-1 and -2, 7.10 and 7.16, respectively, were high, because of the accumulation of potassium salts during the preparation of these two wood fractions. On account of their low solubility in acidified methyl alcohol, these salts are removed from the hemicelluloses with difficulty. The percentage of ash in the wood residue after removal of hemicelluloses-1, 8.6, was high for the same reason. These salts can be removed by washing with water; but, since the residue was to be treated subsequently with sodium chlorite for delignification, thorough washing was unnecessary at this stage, so long as a correction was made for the ash. Salts in the partially delignified wood residue and the cellulose residue after the removal of hemicelluloses-2 are not excessive.

Lignin. Hemicelluloses-1 were bleached with sodium chlorite to remove some lignin that was dissolved along with hemicelluloses-1 by potassium hydroxide. The wood residue after the removal of hemicelluloses-1 contained 26.55% of lignin, which was the major portion of the lignin in the original wood. After the lignin in the wood residue had undergone the sodium chlorite treatment for preparing holocellulose by the sodium chlorite method (*14*), it became fairly soluble, even though treated insufficiently for complete removal. Its incomplete removal explains the reason that some lignin remained in the partially delignified wood residue (Table I) in the hemicelluloses-2, and in the cellulose residue resulting from the isolation of hemicelluloses-2.

Methoxyls. The percentage of methoxyl is 2.15 in hemicelluloses-1 and 3.03 in hemicelluloses-2. In hemicelluloses-1, the methoxyl is associated with the uronic acids; whereas in hemicelluloses-2, part of it is associated with the uronic acids and the remainder with the lignin present in the hemicelluloses. Methoxyl values also appear in the other wood fractions because of the presence of lignin and uronic acids, both of which contain methoxyls.

Pentosans and Uronic Acids. Other significant data in Table I are the percentages of pentosans and uronic acids in hemicelluloses-1 and -2. It may be noted in columns 7 and 8 that the sum of these two components is equivalent to approximately 93.0% (76.6 + 16.7 = 93.3) of hemicelluloses-1. The sum of the values for the same two components plus lignin in hemicelluloses-2 is 92.7% (77.7 + 9.8 + 5.2 = 92.7). The materials unaccounted for in the two hemicelluloses are mainly hexosans, which on hydrolysis are converted to hexose sugars (*6*).

Materials other than hemicelluloses were removed from the wood during extraction of the hemicelluloses. For convenience in tracing these losses, the data in Table I have been recalculated, based on the weight of the oven-dry wood, and recorded in Table II.

It may be noted in Table II that 28.8% of the wood was removed in the preparation of hemicelluloses-1. Of this amount, 14.6% on ash-free, lignin-free basis was recovered and weighed as hemicelluloses, leaving a discrepancy of 14.2%. A slight difference existed between the actual percentage of hemicelluloses-1 recovered and the quantitative analysis of the material. Analysis shows 11.19 pentosans + 2.43 uronic acids = 13.62% as compared with 14.6%. A good share of the 14.2% discrepancy can be accounted for by enlisting some data on the composition of the sugar maple wood given in the section on features of the method. During the extraction of the wood for hemicelluloses-1 the following percentages of materials were also removed: 4.20 extractives + 3.60 acetyl + 2.72 lignin = 10.52, leaving 3.68% (14.2 − 10.52 = 3.68) that did not show up in the analysis.

The composition of the material removed from the wood residue in preparing the partially delignified wood residue is of interest. This removed material is 18.7% of the wood (Table II, column 3) and is the difference between the weights of the two wood residues. Further, the differences between the analysis of the wood residues are: 16.43 lignin + 2.16 pentosans + 0.37 uronic acid = 18.96%, which checks well with the difference between the actual weights of the two wood fractions.

The materials in the partially delignified wood residue in Table

Table III. Effect of Noncarbohydrate Substances on Color Reaction

Added Substance	Description of Added Substance	Amount of Added Substance, Mg.	Formation of Color In H_3PO_4 alone	Formation of Color In H_3PO_4 and glucose	Interference in Reaction of Glucose with Pyrocatechol
Gelatin	Eastman, purified	50	n	n	n
Albumin	Armour, bovine plasma, crystalline	50	Pink	Pink	i
Edestin	3 times recrystallized	50	n	n	n
β-Lactoglobulin	Electrophoretically pure	50	n	Brown	i
Amino acid	Mixture used by (3) with supplement of methionine, no tryptophane	50	n	n	n
Tryptophane	....	0.5	g	Yellow	i(red)
Glucosamine	Recrystallized hydrochloride	3	n	n	n
Purine	Uracil, adenine, uric acid, xanthine, hypoxanthine, guanine	2	n	n	n
Polyhydric alcohol	Sorbitol, mannitol, adonitol, inositol	1	n	n	n
Fatty acid	Palmitic, stearic	2	n	n	n
Salt	NaCl, ammonium sulfate	10	n	n	n
Nitrite	$NaNO_2$	1	Brown	Brown	i

n = no formation of color, or does not interfere in color test.
i = interferes.
g = green fluorescence.

common aldohexoses (glucose, galactose, and mannose) to afford a clear-cut differentiation between them. The ratio, while sensitive to differences of configuration within the sugar unit, is independent of the nature of the interglucosidic linkage, the polymerization degree of the sugar unit, and the carbohydrate concentration. While it was difficult to obtain good reproduction of the absolute amount of color formed by a given sugar, the ratio $\epsilon_{S43}/\epsilon_{S50}$ remained constant within ±7% (see Tables I and II) with any given procedure.

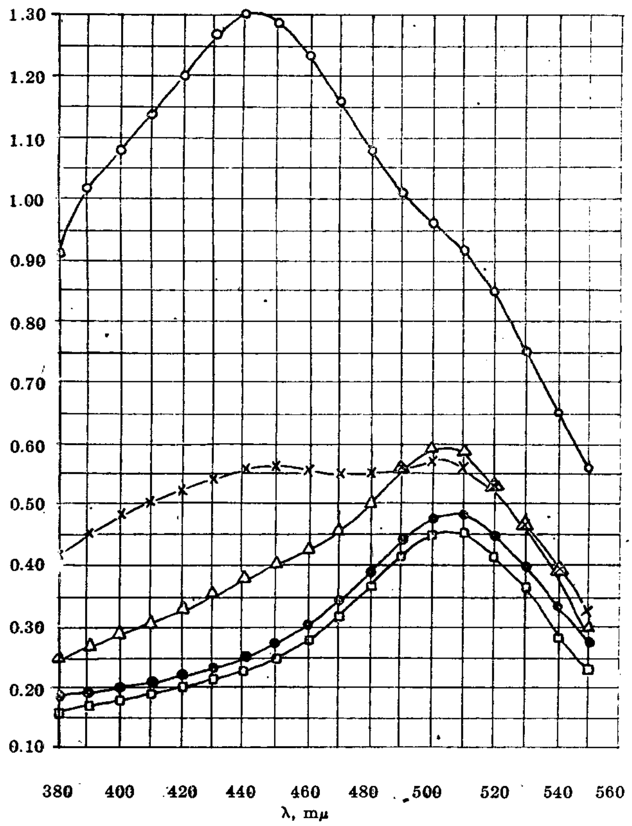

Figure 2. Colors Formed by Reaction of Hexoses with Pyrocatechol

Extinction values measured with Beckman spectrophotometer
Heating time, 15 minutes

●. Glucose
×. Galactose
○. Mannose
} Aldohexose concentration, 0.4 mg. per ml.

△. Fructose
□. Sorbose
} Ketohexose concentration 0.04 mg. per ml.

The method here proposed is valid as a means of identifying glucose only if no other color-forming substance is present in the test material. Common pentoses (*d*- and *l*-arabinose, ribose, xylose, lyxose, and rhaminose) when heated in the pyrocatechol reagent produce colors which are intermediate in tone between the red-brown given by galactose and the lilac given by glucose (see Table II). Moreover, two ketoses (fructose and sorbose) and one pentose (xylose) yield colors which are not certainly distinguishable in terms of $\epsilon_{S43}/\epsilon_{S50}$ from the color given by glucose (cf. Figure 2 and Table II). It is particularly fortunate that the presence of nonglucose sugars (hexoses and pentoses) is revealed by their color in the first step of the standard procedure—i.e., on heating in phosphoric acid alone. Specific testing for presence of these sugar interferants is therefore unnecessary. Glucuronic acid on heating with pyrocatechol forms a red-brown color different from that given by glucose. Like the latter, however, it does not form color on heating with phosphoric acid alone. It is desirable therefore to demonstrate absence of glucuronic acid from the test material by an appropriate independent method.

An identification of glucose on the basis of behavior in the pyrocatechol–phosphoric acid test is necessarily of a presumptive nature. It is always possible that units which are different from glucose but behave in the test in a manner similar to glucose can be present in a biological material.

Influence of Noncarbohydrate Substances on the Color Reaction. Observations concerning the effect of certain groups of noncarbohydrates on the color reaction have been assembled in Table III. It is noteworthy that both tryptophane and nitrite interfere with the test. The absence of interfering color formation in the presence of any amino acid, with the exception of

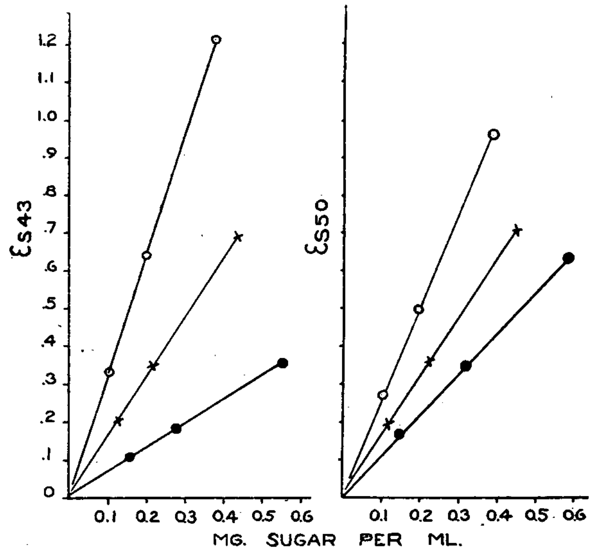

Figure 3. Reactions of Aldohexoses with Pyrocatechol

Heating time, 15 minutes
○. Mannose
×. Galactose
●. Glucose

tryptophane, is an important merit of the present method. It can be expected, therefore, that a tryptophane-free protein such as gelatin will not be an interferant, and this prediction is in fact confirmed. It is evident, furthermore, that the reaction can also be applied safely in the presence of certain proteins which contain tryptophane—e.g., edestin. Yet clearly caution is indicated where the test is being applied on an unknown protein material in which tryptophane can be demonstrated. As may be seen from Table III, both plasma albumin and β-lactoglobulin, interfere with the glucose test.

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Systematic Qualitative Tests for Certain Acidic Elements in Organic Compounds

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A system for the detection of nitrogen, chlorine, bromine, iodine, arsenic, sulfur, and phosphorus in a single 1-mg. sample of an organic compound and for carbon and fluorine in separate 1-mg. samples is described. The procedures are applicable to compounds whose boiling points are greater than approximately 60° C. and any of the above elements can be detected when present to the extent of 1 to 5% of the sample weight.

ONE of the most sensitive and reliable qualitative tests for the presence of nitrogen in organic compounds is the modified Emich test (*1, 4, 5*) described by Johns (*3*). In this test the sample is pyrolyzed in the presence of calcium oxide and zinc and the liberated ammonia is detected with the aid of litmus. Because of the general applicability of this test it appeared desirable to exploit the pyrolytic technique, so that a single ignition could be used not only for the detection of nitrogen but also for the systematic qualitative identification of certain other acidic elements. Early in 1944 a system was developed in these laboratories which provided for the qualitative detection of nitrogen, chlorine, bromine, iodine, sulfur, phosphorus, and arsenic; an outline of this system is shown in Table I.

SYSTEMATIC TESTS

A. Combustion of Sample and Test for Nitrogen. A combustion tube is prepared from a freshly cleaned 12-cm. length of Pyrex tubing 3 mm. in outside diameter by constricting a 2- to 3-mm. portion of the tube to an inside diameter of 0.5 to 0.7 mm. at a distance of 3 cm. from one end of the tube. Acid-washed and freshly ignited asbestos is introduced into the long arm of the combustion tube and is pressed firmly into the near side of the constriction with the aid of a clean glass rod until a plug 2 to 3 mm. in length is obtained.

A mixture of equal parts of calcium oxide, ordinarily prepared by the ignition of calcium oxalate, and 80-mesh zinc powder (sulfur- and arsenic-free) is introduced in small portions, and with tapping, into the long arm of the combustion tube until a 20-mm. column of the mixture is in position immediately adjacent to the asbestos plug. The liquid or solid sample contained in a 2- to 3-mm. segment of a 0.5-mm. inside diameter thin-walled capillary tube 10 to 15 mm. in length is placed on top of the calcium oxide–zinc column and the end of the long arm of the combustion tube is sealed with the aid of a forceps. The open end of the combustion tube is inserted into a 4-cm. length of 5-mm. outside diameter Pyrex tubing for a distance of approximately 1 cm. and in the other end of the sleeve is placed a strip of red litmus paper approximately 3 mm. in width. Since ordinary red litmus paper may not be sufficiently sensitive, strips of ordinary blue or neutral litmus paper are suspended in distilled water and just enough 1 *F* perchloric acid is added to change the color of the paper to pink. The papers are then washed with distilled water until a treated paper when pressed against a piece of neutral litmus paper will not turn the latter red. The prepared papers are pressed between soft filter papers and then stored in a moist condition in a sealed container.

The combustion tube assembly prepared as described above is placed on a wire gauze bearing a 10 × 30 mm. hole, in such a way that the portion of the tube bearing the calcium oxide–zinc mixture is over the hole. The asbestos plug in the combustion tube is first heated to a dull red glow with a small sharp flame from a Bunsen burner, and the burner is moved toward the sealed end of the tube so as next to heat the calcium oxide–zinc zone to glowing and, finally, the space bearing the sample. This heating operation need not consume more than 2 minutes. The presence

Table I. Systematic Detection of Nitrogen, Halogen, Arsenic, Sulfur, and Phosphorus in Organic Compounds

A. Fuse 1-mg. sample with Zn and CaO. Test gas with litmus
Gas: NH_3 (blue litmus color: nitrogen present) Residue: CaI_2, $CaBr_2$, $CaCl_2$, $Ca_3(PO_4)_2$, CaO, ZnI_2, $ZnBr_2$, $ZnCl_2$, ZnS, Zn_3As_2, $Zn_3(PO_4)_2$, Zn
B. Leach residue with water
Solution: Ca^{++}, I^-, Br^-, Cl^-. Treat separate portions as indicated in B-1, B-2, and B-3 Residue: $Ca_3(PO_4)_2$, CaO, ZnO, ZnS, Zn_3As_2, $Zn_3(PO_4)_2$, Zn
C. Add $HClO_4$

B-1. Add $AgNO_3$ and HNO_3	B-2. Add chloramine-T, fluorescein, and acetic acid	B-3. Add starch, $HC_2H_3O_2$, and $NaNO_2$	Gases: H_2S, AsH_3 C-1 Collect gases separately in $HgCl_2$ and $Pb(C_2H_3O_2)_2$	Solution: H_3PO_4, Zn^{++}, Ca^{++}, $HClO_4$ D. Add portion to $(NH_4)_2MoO_4$ and HNO_3 on test paper. Add benzidine and $NaC_2H_3O_2$
Ppt.: AgI, AgBr, AgCl (halogen present)	Pink color: eosin, tetraiodofluorescein (bromine and/or iodine present)	Starch-iodine color (iodine present)	Ppt.: PbS (black, sulfur present), $HgAsH_2Cl$ (yellow, arsenic present)	Blue color: phosphorus present.

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of nitrogen in the sample is indicated by a change in color from pink to blue at the end of the litmus strip nearer the open end of the combustion tube. Any color obtained should be compared with that obtained from a blank test. Although exposed strips of litmus very quickly lose their blue color when allowed to stand in contact with air, comparisons may be made as long as 15 minutes after a combustion if the paper strips are placed between two microscope slides immediately after exposure.

B-1. Tests for Halogen. The short arm of the combustion tube is sealed and the long arm opened near the tip. The newly sealed end of the tube is warmed and as the tube cools several drops of water are added, so that the water is slowly drawn into the calcium oxide–zinc mixture. After 10 to 15 seconds the tube is centrifuged to collect the aqueous solution in the closed end of the tube. The combustion tube is cut about 5 mm. above the water meniscus and the aqueous solution reserved for subsequent tests. The solid residue contained in the other portion of the tube is carefully warmed to remove any water and set aside for subsequent operations.

In a 1- to 1.5-mm. thin-walled capillary a 4- to 5-mm. column of the aqueous extract is allowed to react with a 3- to 4-mm. column of a solution 0.5 *F* in silver nitrate and 3 *F* in nitric acid. The formation of a white or light yellow precipitate within 30 seconds indicates the presence of chloride, bromide, or iodide. With properly prepared reagents, blank tests will give only a very slight turbidity.

Table II. Nitrogen Test

Test Equivalent to That Given by Nitrogen, Taken as Ammonium Chloride

	A. 5 to 10 γ N	B. 10 to 30 γ N	C. More than 30 γ N
Amines	Arsanilic acid 2-Aminopyridine Quinoline ethiodide	*n*-Heptylamine *N*,*N*-diethylcyclohexylamine Tris(β-chloroethyl)amine *N*-ethylpyrrole Pyridine 2-Chloropyridine 2-Bromopyridine 3-Bromopyridine Tetra-*n*-butylammonium iodide	2-Amino-*n*-octane *o*-Bromoaniline 2-Amino-4-chlorothiophenol hydrochloride *N*-methyl-ethylamine hydrochloride Dibenzylamine *N*-ethyl-diethanolamine hydrochloride *N*-methyl-bis(β-chloroethyl)-amine *N*-ethyl-bis(β-chloroethyl)-amine *N*,*N*-dimethyl-*p*-bromoaniline
Amides	...	*n*-Heptamide *N*-acetyl-α-naphthylamine *m*-Acetamidobenzoic acid *N*,*N*-diethylchloroacetamide Thioacetanilide Ethyl *N*-phenylcarbamate Ethyl *N*,*N*-di-*n*-butylcarbamate Benzenesulfonamide *o*-Toluenesulfonamide	Propionamide *n*-Butyramide Chloroacetamide Trichloroacetamide *N*-acetyl-β-methoxyethylamine *N*,*N*-diethylacetamide *N*,*N*-amylsuccinimide *n*-Butyloxamate *N*-methylurea *N*-acetylurea *N*-acetyl-*N'*-methylurea *N*,*N'*-di-*n*-butylthiourea Ethyl carbamate *n*-Propyl carbamate *n*-Butyl carbamate *n*-Amyl carbamate β-Ethoxyethyl carbamate Ethyl *N*-methylcarbamate Ethyl *N*-ethylcarbamate Ethyl *N*,*N*-diphenylcarbamate Ethyl *N*-phenyl-*N*-benzylcarbamate Sodium *N*,*N*-diethyldithiocarbamate *p*-Aminobenzenesulfonamide Dichloramine-T
Nitriles	...	*n*-Butyronitrile Chloroacetonitrile α-Bromobenzylcyanide Benzoylacetonitrile	Acetonitrile Furonitrile Succinonitrile Methylcyanoacetate *p*-Nitrophenylacetonitrile β-Hydroxy-γ-chloro-*n*-butyronitrile Ethyl β-phenyl-α-cyanoacrylate *N*,*N*-di-*n*-butylcyanamide *N*,*N*-diallylcyanamide Dicyandiamide Cyanogen bromide
Oximes	...	*n*-Butyraldoxime α-Benzil monoxime	*n*-Heptaldoxime Acetone oxime Cyclohexanone oxime Biacetyl monoxime
Nitro compounds	...	Chloropicrin	Bromopicrin 2-Methyl-2-nitro-1-propanol *o*-Dinitrobenzene 4,4'-dinitrobiphenyl *m*-Nitrophenylarsonic acid
Nitroso compounds	*N*,*N*-diphenylnitrosoamine	Nitrosobenzene *N*-methyl-*N*-phenylnitrosoamine	2-Nitroso-3-hydroxy-toluene *o*-Nitrosonitrobenzene *N*-nitrosopiperidine Ethyl *N*-nitroso-*N*-ethylcarbamate
Nitrates, nitrites	...	Ethyl nitrate	Butyl nitrate Sodium nitrate Sodium nitrite
Miscellaneous heterocyclic compounds	Phenarsazine chloride	Benzothiazole Benzoxazole	2-Aminobenzothiazole *o*-Benzoicsulfimide 1-Acetyl-2-thiohydantoin
Miscellaneous	Formyl diphenylamine Azobenzene	Benzalaniline Benzalmethylamine Benzalazine *N*,*N*-diphenylformamidine Diazoaminobenzene	Ethylene thiocyanate Potassium thiocyanate 1-Aminoguanidine sulfate

B-2. Test for Bromide or Iodide. If a positive test for halogen is obtained (B-1) a 5- to 6-mm. column of the aqueous extract is placed in a 1- to 1.5-mm. capillary tube and a 3- to 4-mm. column of freshly prepared 0.0035 *F* aqueous chloramine-T is added, followed by a 3- to 4-mm. column of a 50% aqueous ethanol solution 0.00075 *F* in fluorescein and 0.12 *F* in acetic acid and then another 3- to 4-mm. column of 0.0035 *F* chloramine-T. When viewed against a white background, the formation of a pink color is indicative of the presence of bromide or iodide. No color should be obtained in blank tests on properly prepared reagents.

B-3. Test for Iodide. If a positive test for bromide or iodide is obtained (B-2), a 3- to 4-mm. column of the aqueous extract is placed in a capillary tube and to it is added a 3- to 4-mm. column of a reagent freshly prepared by mixing equal columns of 0.5% starch solution, 1 *F* sodium nitrite, and 6 *F* acetic acid. The formation of a blue or black color indicates the presence of iodide. No color should be obtained in blank tests.

C-1. Test for Sulfur and Arsenic. Cut open the combustion tube near the middle of the fusion mixture and by gentle tapping transfer all the mixture into the 3 × 15 mm. depression of a culture-type microscope slide. A glass ring 18 mm. in inside diameter and 15 mm. high is then placed around the depression. With a wax pencil a line is drawn across the center of a cover slip and on one side of the line is placed a drop of 1 *F* lead acetate and on the other a drop of 0.1 *F* mercuric chloride. The cover slip is inverted and placed in position on the glass ring immediately after the addition of 4 drops of 9 *F* perchloric acid to the fusion mixture. The formation of a brown or black precipitate in the lead acetate drop after 2 to 3 minutes is indicative of the presence of sulfur; however, in the absence of arsenic the presence of sulfur may also be indicated by the formation of a white precipitate ($HgCl_2 \cdot 2HgS$) in the mercuric chloride drop.

The probable presence of arsenic is indicated by the formation of a yellow or brown precipitate in the drop of mercuric chloride. If the original sample contains tripositive or elementary phosphorus, some phosphorus may be present as calcium or zinc phosphide after fusion and when the perchloric acid is added to the fusion mixture phosphine may be liberated and may cause an orange-brown precipitate to form in the mercuric chloride. For this reason an orange or brown precipitate in the mercuric chloride drop is not necessarily proof of arsenic, though most of the tripositive phosphorus compounds examined do not give a detectable precipitate. With suitably selected zinc metal no significant amounts of sulfur or arsenic should be found in blank tests.

D. Test for Phosphorus. A test paper is prepared by placing a few drops of a solution 0.03 *F* in ammonium molybdate, $(NH_4)_6Mo_7O_{24}$, and 3.9 *F* in nitric acid on a Whatman No. 1 or similar filter paper and drying the paper at 80° to 90°. A 5- to 8-mm. column of the perchloric acid solution remaining after the operations described in C-1 and contained in a 1- to 1.5-mm. capillary tube is transferred to an impregnated section of the test paper. Then in succession are added a 5-mm. column of a solution, 0.0027 *F* in benzidine and 1.8 *F* in acetic acid, and an equal volume of saturated aqueous sodium acetate. The presence of phosphorus is indicated by the formation of a blue spot; this should always be compared with that obtained in a blank test.

RESULTS OBTAINED WITH SYSTEMATIC SCHEME

A. Nitrogen Test. Experiments have shown that this test will detect as little as 2 to 3 micrograms of nitrogen taken as an ammonium salt or about 5 micrograms taken as a nitrate. With suitably prepared reagents a blank test will give at the most only a short zone of pale lavender color on the litmus paper.

A large number of compounds were tested for the presence of nitrogen in order to determine whether or not the test could be relied upon with nitrogen-containing compounds of widely varying structure.

In general a 1-mg. sample of the substance was taken and the test recorded as: (A) equivalent to test given by 5 to 10 micrograms of nitrogen taken as ammonium chloride; (B) equivalent to test given by 10 to 30 micrograms of nitrogen taken as ammonium chloride; and (C) equivalent to test given by more than 30 micrograms of nitrogen taken as ammonium chloride. The results of these tests are given in Table II.

In no case was a negative test obtained despite the relatively great variation in the types of the compounds tested. It therefore appears that the test described is generally applicable.

Halogen Tests (B-1, B-2, B-3). The tests for the halogens are based upon the assumption that only one halogen is present; if more than one halogen is present, only that one which has the higher atomic weight will be specifically detected. The sensitivity of the halide tests is limited by the purity of the reagents employed. However, no difficulty was experienced in preparing reagents which gave only a very slight turbidity with the silver nitrate–nitric acid reagent and no test for bromine and iodine. Satisfactory positive tests were obtained with 5-microgram quantities of chloride, bromide, and iodide in procedure B-1, with 5 micrograms of bromide and iodide in procedure B-2, and with 5 micrograms of iodide in procedure B-3. With a 1-mg. sample satisfactory halide tests were obtained with procedure B-1 for all halogen-containing compounds examined. In all cases where bromine or iodine was present a satisfactory test was obtained using procedure B-2, and when iodine was present a satisfactory test was obtained using procedure B-3. When bromine or iodine were absent the tests in procedures B-2 and B-3 were uniformly negative. The compounds listed in Table III were among those examined.

Table III. Halogen Tests

	Chlorine-Containing Compounds	
n-Butyl chloride	β-Chloroethyl-*p*-toluenesulfonate	Chloroform
2-Chloropyridine	Dichloramine-T	1,2-Dichloro-*n*-butane
2,3-Dichlorodioxane	Bis(β-Chloroisopropyl) ether	Diphenylselenium dichloride
1,1,1-Trichloroethane	Phenyl mercuric chloride	Tetrachloroethylene
p-Toluenesulfonyl chloride	Trichloroacetamide	*N*-methyl-bis(β-chloroethyl)amine
N-ethyl-bis(β-chloroethyl)amine	Tris(β-chloroethyl)amine	α-Chloroacetophenone
Bis(β-chloroethyl) sulfide	Bis(β-chloroethyl) sulfone	Chloropicrin
Ethyl dichloroarsine	β-Chloroethyl dichloroarsine	1,1,2,2-Tetrachlorodinitroethane
	Bromine-Containing Compounds	
Benzalacetophenone dibromide	*o*-Bromoanisole	*N*,*N*-dimethyl-*p*-bromoaniline
Bromopicrin	2-Bromopyridine	3-Bromopyridine
2-(β-butoxyethoxy)-ethyl bromide	Isobutylene bromide	4,4′-Dibromodiphenyl sulfone
1,2-Dibromoethylene	Epibromohydrin	Ethyl dibromoacetate
α-Bromoacetophenone	Phenylmercuric bromide	Sodium 2-bromoethanesulfonate
4-Bromoacetylbiphenyl	α-Bromobenzylcyanide	Cyanogen bromide
Ethyl bromoacetate		
	Iodine-Containing Compounds	
Iodoform	Iodosobenzene	*o*-Iodotoluene
Quinoline ethiodide	2,4,6-Triiodobenzene	

Table IV. Sulfur Tests

	Test Equivalent to That Given by Sulfur, Taken as Sodium Sulfate	
	A. 20 to 40γ S	B. More than 40γ S
Mercaptans, sulfides, disulfides	2-Mercaptobenzoxazole	Thioglycolic acid
	Phenyl sulfide *p*-Tolyl ethyl sulfide	Thio-β-naphthol 2-Amino-4-chlorothiophenol hydrochloride
	p-Tolyl methyl sulfide	Thiodiglycol Thiodiglycolic acid Bis-(β-chloroethyl)sulfide Benzyl sulfide Isobutyl disulfide Benzyl disulfide Phenyl disulfide Phosphorus sulfide (P_4S_7) Phosphorus sesquisulfide (P_4S_3)
Sulfoxides, sulfones	*n*-Propyl sulfone	Phenyl sulfoxide
	Phenyl-*p*-tolyl sulfone	*n*-Butyl sulfone Bis-(β-chloroethyl) sulfone 4,4′-dibromodiphenyl sulfone
Sulfonic acids and derivatives	Sodium allylsulfonate	*o*-Toluenesulfonamide
	Sodium 2-bromoethanesulfonate	*p*-Aminobenzenesulfonamide Dichloramine-T
	β-Chloroethyl toluenesulfonate *p*-Toluene sulfonyl chloride Benzenesulfonamide	*o*-Benzoicsulfimide
Sulfates, sulfites	1-Aminoguanidine sulfate	*n*-Propyl sulfate Sodium sulfate Ammonium sulfamate *n*-Butyl sulfite
Thiocyanates	Benzyl thiocyanate Potassium thiocyanate	Ethyl thiocyanate *n*-Butyl thiocyanate Ethylene thiocyanate Perthiocyanic acid
Miscellaneous	Tri-*o*-cresyl thiophosphate	Thioacetanilide *N*,*N*′-di-*n*-butylthiourea
	Triphenyl thiophosphate	Sodium diethyl dithiocarbamate
	Ethyl thioacetate Trithiomethylene	Benzoyl disulfide

Sulfur Test (C-1). The sensitivity of this test appears to be limited by the purity of the zinc metal used in the preparation of the combustion mixture. It was found that a sample of Baker's "zinc metal, granular 80-mesh" was sufficiently free of sulfur to permit the unambiguous detection of 10 micrograms of sulfur originally present as sodium sulfate. A number of sulfur-containing compounds were examined using 1-mg. samples and the intensity of the test was recorded as: (A) equivalent to test obtained with 20 to 40 micrograms of sulfur taken as sodium sulfate, and (B) equivalent to test obtained with more than 40 micrograms of sulfur taken as sodium sulfate. The results of these tests are given in Table IV.

In no case was a negative test obtained with a sulfur-containing compound and in view of the variety of compounds examined it appears that the sulfur test described is generally applicable.

Arsenic Test (C-1). If phosphorus is absent, the test for arsenic will provide for the unambiguous detection of as little as 5 micrograms of arsenic originally present as sodium arsenate. The presence of phosphorus may lead to spurious results. Therefore, if phosphorus is found to be present, caution should be

Table V. Fluorine Test

A. Equivalent to 6 to 10 γ of of Fluoride Ion	B. Equivalent to More than 10 γ of Fluoride Ion
Difluoroacetonitrile	*n*-Butylsulfonyl fluoride
β-Fluoroethyl chlorosulfonate	β-Chloroethyl fluoroacetate
β-Fluoroethylnitrite	Bis(β-chloroethyl) fluorophosphate
	Diethylamino phosphonyl fluoride
	p,p'-Difluorobiphenyl
	N,N-diethylfluoroacetamide
	Diisopropylfluorophosphate
	N,N'-tetramethylamino-phosphoryl fluoride
	β-Fluoroethanol
	Bis(β-fluoroethyl)carbonate
	p-Fluoroaniline
	p-Fluoroanisole
	β-Fluoroethylchloroformate
	β-Fluoroethylchloromethyl ether
	Bis(β-fluoroethyl)-β-fluoroethylphosphate
	Methyl fluoroacetate

exercised in accepting a positive arsenic test as conclusive evidence of the presence of this latter element. Using *ca.* 1-mg. samples satisfactory tests were obtained with all arsenic-containing compounds examined, which included arsanilic acid, *m*-nitrophenylarsonic acid, phenarsazine chloride, phenarsazine cyanide, phenyldichloroarsine, ethyldichloroarsine, and β-chloroethyldichloroarsine.

Phosphorus Test (D). As little as 5 micrograms of phosphorus, originally present as sodium phosphate or phosphorus trichloride, can be detected with this test, provided care is taken to select reagents which are essentially free of phosphorus. Using a 1-mg. sample satisfactory tests were obtained with all phosphorus-containing compounds examined. These included red phosphorus, phosphorus sesquisulfide, phosphorus sulfide, phosphorus trichloride, sodium β-glycerophosphate, and tri-*o*-cresyl thiophosphate.

QUALITATIVE TEST FOR CARBON

A method suitable for the detection of about 10 micrograms of carbon was developed which was based upon the wet combustion of a 1-mg. sample with a mixture of iodic, chromic, sulfuric, and phosphoric acids and subsequent detection of the carbon dioxide formed by precipitation as barium carbonate.

Carbon Test. A tip 0.2 to 0.3 mm. in inside diameter and 10 mm. long is formed on one end of a 15-cm. length of 1.5- to 2.5 mm. inside diameter soft glass thin-walled capillary tubing previously prepared from 30-mm. glass tubing thoroughly cleaned with a hot chromic acid–sulfuric acid mixture. The tube is then gently heated, in the flame of a microburner, at a point *ca.* 5 cm. from the tip, so as to cause the tube to bend by its own weight into a canelike form. A pipet is also prepared by forming a tip 0.5 mm. in outside diameter and *ca.* 8 cm. long on a piece of 1.0- to 1.5-mm. thin-walled capillary tubing. The combustion mixture used was prepared by carefully mixing 33 ml. of 85% phosphoric acid and 67 ml. of 30% fuming sulfuric acid in a 250-ml. g.s. flask and then adding 6.0 grams of chromium trioxide and 1.0 gram of potassium iodate. The contents of the unstoppered flask were heated, with gentle agitation, until the temperature reached 140° to 150°. The flask was then covered with an inverted beaker and allowed to cool to 25°, whereupon it was stoppered and contamination of the rim of the flask by dust prevented by inverting a beaker over the neck of the flask.

With the aid of the pipet described above a 25-mm. column of the combustion mixture is placed in the longer arm of the cane tube. The tip of the short arm of the cane tube is allowed to come in contact with a drop of a centrifuged solution 2 *F* in sodium hydroxide and saturated with barium chloride until a column 5 to 7 mm. in length is present in the larger part of the arm. The short arm of the cane tube is then sealed by rapidly passing the tip through the edge of a burner flame. The sample contained in a 0.5 mm. inside diameter capillary tube (3- to 4-mm. column = approximately 1 mg.) is inserted into the long arm of the cane tube and placed in position within a few millimeters of the column of combustion mixture. The long arm of the cane tube is then sealed at a point 10 to 20 mm. from the open end. The sealed cane tube is hung on the edge of a 15-ml. centrifuge tube and centrifuged gently to drive the sample and combustion mixture to the bottom of the tube. The portion of the cane tube containing the sample and combustion mixture is heated in a boiling water bath for 3 to 5 minutes. If a white crust is formed on the surface of the barium hydroxide solution the tube is taken from the bath and gently centrifuged until the precipitate is driven to the bottom of the short arm. The tube is replaced in the boiling water bath and after a minute a precipitate will reappear on the surface of the barium hydroxide solution if carbon is present.

Blank tests often may produce a small amount of precipitate on the surface of the barium hydroxide solution, but this precipitate does not reappear after one centrifuging. Positive tests for carbon in a 1-mg. sample of an organic compound will eventually lead to the formation of a heavy precipitate throughout the solution contained in the short arm of the cane tube, provided the cane tube is periodically centrifuged.

RESULTS OBTAINED WITH CARBON TEST

A 1-mg. sample of bromopicrin, containing approximately 10 micrograms of carbon, gave an unambiguous positive test. However, acetic acid and compounds which yield acetic acid as the only carbon-containing compound upon hydrolysis may give only a poor test with 3 to 5 minutes' heating. In no case except that of acetic acid did a carbon-containing compound fail to give a satisfactory test, even though such difficultly oxidizable materials as benzene, pyridine, and graphite were examined. The other compounds tested were: acetylurea, arsanilic acid, benzyl chloride, *o*-bromoaniline, carbon tetrachloride, β-chloroethyl *p*-toluenesulfonate, 2-chloropyridine, diazoaminobenzene, dichloramine-T, 1,2-dichloro-*n*-butane, bis(β-chloroethyl) carbonate, dioxane, *N,N*-diphenylnitrosoamine, ethanol, fluorobenzene, methanol, *m*-nitrophenylarsonic acid, quinoline ethiodide, tetra-*n*-butylammonium iodide, tetrachloroethylene, tetralin, and triphenyl thiophosphate.

The technique used in the carbon test is generally applicable to all cases involving the liberation of a gas and its subsequent capture in a suitable reagent. For example, its application to the detection of α-amino acids by oxidation with ninhydrin to give carbon dioxide (*6*) is obvious.

QUALITATIVE TEST FOR FLUORINE

The presence of fluorine in organic compounds can be detected by decomposing a 1-mg. sample with a mixture of iodic, chromic, sulfuric, and phosphoric acids, collecting the hydrogen fluoride in a hanging drop of water, and then examining the aqueous solution for the presence of fluoride by taking advantage of the insolubility of thorium fluoride and the intense red color of the lake of alizarin sulfonate adsorbed on thorium hydroxide. If fluorine is absent the lake forms and a red color is observed. If fluorine is present, thorium fluoride is formed and no color is observed.

Fluorine Test. Approximately 1 mg. of the liquid or finely powdered solid sample is placed in the 3 × 15 mm. depression of a culture-type microscope slide and a glass ring is placed around the depression as in the previously described arsenic-sulfur test. Ten drops of the iodic-chromic-sulfuric-phosphoric acid mixture are added to the sample and the ring is immediately covered with a 2.5-cm. watch glass, on the under side of which is a hanging drop of water. The assembly is allowed to stand for 5 minutes and then placed on a 7.5-cm. (3-inch) iron ring. Two drops of water are placed on the top side of the watch glass, to prevent subsequent evaporation of the hanging drop, and the bottom of the slide is carefully heated, with a small flame, until the mixture in the cell begins to fume and then for 30 seconds longer. The hanging drop is removed with a capillary pipet and transferred to a 10 × 75 mm. test tube. One drop of 6 *F* formic acid and one drop of 2% hydrazine hydrate are added and the mixture is heated to 50° to 60°. After 20 seconds 1 ml. of water, one drop of 3 *F* sodium hydroxide, and two drops of 0.12% ethanolic sodium alizarinsulfonate are added and the solution is thoroughly mixed. A similar solution is prepared for comparison purposes containing all the reagents used. To each tube one drop of 0.0005 *F* thorium nitrate is added, the solution is mixed by shaking the tubes gently, and the colors are compared. If fluorine is present the tube containing the hanging drop will be yellow and the comparison tube pink. One drop (0.05 ml.) of 0.0005 *F* thorium nitrate is equivalent to *ca.* 2 micrograms of fluoride and if fluorine is present the amount in the hanging drop can be estimated by the dropwise addition of the thorium nitrate solution.

Experiments have shown that, depending on the nature of the compound, 15 to 50% of the fluorine present in the sample is collected as fluoride in the hanging drop. If the sample does not contain bromine or chlorine, the procedure can be simplified by omitting the hydrazine reduction.

RESULTS OBTAINED WITH FLUORINE TEST

One-milligram samples of a number of fluorine-containing compounds were examined and the result of the test was recorded as: (A) equivalent to test obtained with 6 to 10 micrograms of fluoride ion, and (B) equivalent to test given by more than 10 micrograms of fluoride ion. The results are given in Table V.

Negative tests were obtained with 1-mg. samples of β-chloroethyl chlorosulfonate, β-chloroethylisocyanide dichloride, and dimethylchloroarsine.

The system of qualitative analysis described above was used frequently during the war period for the rapid identification of elements in organic compounds and no difficulty was experienced in obtaining unambiguous results. During the past year the system has been used with equal success in a laboratory course given for senior and first-year graduate students.

ACKNOWLEDGMENT

Several of the tests used in the systematic scheme have been based upon tests described by Feigl (*2*). The authors wish to express their appreciation of the assistance given by A. Briglio, D. Brown, G. Holzman, and T. Lee during the course of this work.

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NOTES ON ANALYTICAL PROCEDURES . . .

Determination of Small Amounts of Sodium Bicarbonate in Sodium Carbonate

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THE procedure commonly employed for determining sodium bicarbonate in sodium carbonate is that of Winkler, in which the bicarbonate is neutralized with an excess of standard base, barium chloride is added to precipitate the carbonate ions quantitatively, and the excess of base is determined by titration with standard acid in the presence of the barium carbonate (*3*). For materials in which both carbonate and bicarbonate are present in appreciable quantities, this method is satisfactory. But in soda ash, in which the sodium bicarbonate content seldom exceeds 1% and is usually much less, application of Winkler's method without suitable modification may result in errors as large as 100% of the true sodium bicarbonate content. The precipitation of barium carbonate appears to remove effectively some of the excess base from solution by occlusion in the barium carbonate. [The use of silver nitrate as an external indicator for the titration of sodium bicarbonate with sodium hydroxide in the presence of much sodium carbonate, a method also commonly in use (*1*), is inaccurate. By this method the end point is reached when as much as 0.5% sodium bicarbonate is still not neutralized.]

To correct for this effect when small quantities of sodium bicarbonate are being determined, it has been found necessary in this laboratory to make a blank determination on sodium carbonate that is free from bicarbonate. Such material may be prepared by igniting reagent grade sodium carbonate at 140° C. for 3 hours or at 160° C. for 1.5 hours (*2*).

The procedure employed in this laboratory for determining small quantities of sodium bicarbonate in soda ash is as follows:

Approximately 10 grams of sample, accurately weighed, are transferred to a 250-ml. volumetric flask, dissolved in freshly boiled, cool distilled water, and diluted to the mark. A 50-ml. aliquot of the sample is treated with 5 ml. of 0.1 *N* sodium hydroxide, then with 50 ml. of 1.0 *N* barium chloride that is neutral to phenolphthalein. After thorough mixing the suspension is titrated potentiometrically with 0.1 *N* hydrochloric acid without undue delay, to prevent pickup of carbon dioxide from the atmosphere. The blank determination is performed in an identical manner. It is imperative that identical quantities of sodium hydroxide be used for both sample and blank, since the blank correction is related directly but not linearly to the quantity of excess sodium hydroxide present when the barium carbonate is precipitated. The magnitude of the blank correction has been found to be approximately 0.2% sodium bicarbonate. For reasons not known, the correction varies sufficiently with different reagents, so that it should be measured for each determination unless its constancy has been established. The values cited in Table I were obtained over an interval of nearly two years, using different batches of sodium carbonate and different reagents.

Table I shows results obtained from the analysis of two series of independently prepared synthetic samples. Without the blank correction systematic errors ranging from 15 to over 100% of the actual bicarbonate content are obtained, whereas deviations of the corrected results may be attributed to experimental error.

Table I. Accuracy of Analysis of Sodium Bicarbonate

	Trial I		Trial II	
Present %	Found %	Corrected %	Found %	Corrected %
0.20	0.48	0.24	0.38	0.22
0.40	0.65	0.41	0.57	0.41
0.60	0.81	0.57	0.76	0.60
0.80	1.03	0.79	0.95	0.79
1.00	1.24	1.00	1.16	1.00
Blank	0.24	..	0.16	..

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Determination of Nitrogen Oxides in Air

Permanent Color Standards for Use with Method of Patty and Petty

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A COLORIMETRIC field method for estimating the content of nitrogen oxides in industrial atmospheres has been described by Patty and Petty (*1*). The method is based on the hydrolysis of nitrogen dioxide or tetroxide to nearly equimolecular amounts of nitric and nitrous acids in a reagent containing α-naphthylamine, sulfanilic acid, and acetic acid, with which the nitrite ion reacts to give a red color; nitrous oxide and nitrogen pentoxide are not acted upon by this reagent, but are not commonly encountered in appreciable quantities in industrial atmospheres. A 50-ml. ground-glass syringe (B-D, Yale) serves as container for the reagent, sampling device, reaction vessel, and color comparator tube. A field kit was designed to contain six loaded syringes, six standards (made from a standard sodium nitrite solution), and bottles of solutions of the two reagents.

Since the color produced by the reaction fades considerably upon standing several hours, it is necessary to carry a standard nitrite solution in the kit to make fresh standards daily. This, in turn, necessitates carrying a larger stock of the reagent solutions for making up the color standards and also adds to the time of preparation for each test. It was suggested by Patty and Petty that the use of permanent glass color standards of suitable form would cut down the size of the field kit as well as the time for preparation.

PREPARATION OF PERMANENT STANDARDS

With the aid of a General Electric recording spectrophotometer, the authors found a suitable blend of dyes with which to dye a series of cellophane strips to different depths of color, so as to match a series cf color standards corresponding to 5, 10, 20, 30, 40, and 50 p.p.m. of nitrogen dioxide in 50 ml. of air at 25° C.

Small squares (7.5 × 7.5 cm., 3 × 3 inches) of non-moisture-proof cellophane (du Pont 600) were treated for various lengths of time in the following dye bath:

Calcomine Fast Red 8B[a]	25 mg. per liter
Calcomine Sky Blue FF, Ex. Conc.[a]	0.2 mg. per liter
Sodium chloride	5.25 grams per liter
Total volume of bath	2 liters
Temperature	80° C.

[a] Made by Calco Chemical Division, American Cyanamid Co., 30 Rockefeller Plaza, New York, N. Y.

In order to ensure uniform dyeing, the strips of cellophane were held on special glass frames and the dye bath was kept in motion, so that the strips would not stick to one another. As the strips were removed, they were rinsed in distilled water and stretched over the mouth of a wide-mouthed bottle to dry as a smooth sheet, free from wrinkles. The following results were obtained after the diffusion rates of the two dyestuffs were ascertained by preliminary experiments.

Dyeing Time, Min.	Equivalent P.P.M. of NO_2 per 50 Ml. of Air
2	5
3	10
7	20
11.5	30
17.5	38
25	45

The dyed cellophane strips were laminated with 3 × 5 cm. pieces of cellulose nitrate sheet in such a way that one lengthwise half (1.5 × 5 cm.) of the piece contained the dyed cellophane, while the other half was the clear plastic. The lamination was done by wetting the inner edges of the two sheets of plastic with alcohol, putting the cellophane strip in place, and pressing the edges with a warm iron until bonded.

CALIBRATION OF CELLOPHANE STANDARDS

The cellophane standards were calibrated by comparing with nitrite standards prepared as described by Patty and Petty.

Approximately 10 ml. of the colored solution were placed in the syringe, the solution was agitated so as to wet the ground-glass surface above the solution, and the mounted strip was held in front of the syringe, so that the clear half was over the colored solution, the dyed cellophane over the empty space above the solution, and the boundary just at the surface of the solution. In this way, the blank due to the plastic and the syringe walls was automatically canceled out. Different solution standards, progressively differing by 5 p.p.m., were compared until a match was made, and the strip was then properly labeled. The comparison was made against a background of diffused daylight—i.e., looking through a window at the sky, with a thin sheet of white paper directly behind the syringe and touching it. An artificial source of diffused white light would probably serve equally well.

TEST PROCEDURE

The procedure for testing air for nitrogen oxides is exactly the same as described by Patty and Petty up to the actual evaluation.

After 10 ml. of the mixed reagent have been placed in the syringe, 50 ml. of air drawn in, and the mixture shaken and allowed to stand about 10 minutes, the dyed cellophane standards are compared until the closest match is found.

STABILITY WITH TIME

Two identical sets of cellophane standards were made, one of which was kept in a sealed envelope, while the other was used in the field as occasion demanded for evaluating the nitrogen dioxide content of industrial atmospheres. The latter set was thus given a limited exposure to indoor diffused daylight or artificial light over a period of 2 years. At the end of this time, both sets of cellophane standards were compared with freshly prepared nitrite standards. Any differences in depth of color between the cellophane standards and the fresh sloution standards were imperceptible, and the two sets were likewise practically indistinguishable. It seems safe to conclude, therefore, that these color standards are sufficiently stable for practical purposes. Frequent or prolonged exposure to direct sunlight will cause some degree of fading in practically any dye, and is not recommended. The slight darkening of the cellulose nitrate in the mount, which occurs over a period of time, has no effect on the results obtained, because of the self-contained blank.

EFFECT OF TEMPERATURE

As stated by Patty and Petty, the speed of the color reaction varies inversely with the temperature, the time for maximum development of color being 30 minutes at 4° C., 10 minutes at 25° C., and 5 minutes at 50° C.

While the value of the nitrite solution standards in p.p.m. of nitrogen dioxide by volume is calculated on the basis of tests taken at 25° C., actually a variation of 20° on either side of 25° C. would cause a difference of less than 4 p.p.m. in the 50 p.p.m. standard.

DISCUSSION

The cellophane standards described here have proved satisfactory in field use, and the authors have not looked into the use of other materials. It is possible, however, that the dye medium or mounting, or both, for permanent standards could be made

from other plastics, such as methyl methacrylate, which would **have** less tendency to darken or warp on aging.

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Electrometric Titration of Nitric Acid in Oleum

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AN ELECTROMETRIC method is described for the determination of the amount of nitric acid added to oleum as an antifreeze. Bowman and Scott (*1*) recommend the titration of nitric acid with a standard solution of ferrous sulfate in which the first appearance of the red-brown color of the ferrous nitrosyl sulfate is taken as the end point of the titration. The color of the end point is easily obscured if the oleum is dark in color. This is frequently the case when reclaimed sulfuric acid is used as "drip acid," the sulfuric acid in which sulfur trioxide is absorbed in the manufacture of oleum.

A previous publication (*3*) on the electrometric titration of nitric acid requires the use of a potentiometer and a specially prepared electrode and titration cell. In the present work the authors used the Serfass electron ray titration assembly (*2*) fitted with a platinum-tungsten electrode combination. The advantages of this setup are the convenience, elimination of the interference of the end point by the dark color of the oleum, and elimination of the empirical blank correction of about 0.20 ml. Although the authors used the Serfass assembly in this work, any similar assembly should perform equally well.

ANALYTICAL PROCEDURE

The ferrous sulfate solution is prepared by dissolving 176.5 grams of ferrous sulfate heptahydrate in about 400 ml. of water and adding 500 ml. of 60% sulfuric acid while stirring vigorously. The solution is diluted to 1 liter and is approximately 0.6 *N*. This solution is standardized against 0.5 *N* potassium dichromate in the presence of 10 ml. of 18 *N* sulfuric acid in the manner described below for the determination of nitric acid.

A sample of oleum containing about 0.4 gram of nitric acid is weighed from a Lunge pipet into a 250-ml. beaker containing 100 ml. of concentrated (95%) nitric-free sulfuric acid. The sensitivity control of the titration unit is turned to position eight and the polarization control is set in the off position. The electrodes and mechanical stirrer are placed in the beaker and the solution is mixed thoroughly. The cathode ray tube is adjusted to the closed position by means of the "eye control." The sample is titrated with the ferrous sulfate solution; the first few milliliters cause the eye to open momentarily. Further slow addition brings the eye back to the closed position, and the titration is continued until the eye remains open for 30 seconds.

The nitrosyl sulfuric acid is determined by titration with standard potassium permanganate. A 10-gram sample of the oleum is weighed into a 100-ml. volumetric flask containing about 20 ml. of 95% sulfuric acid. The sample is diluted with sulfuric acid to the mark, and a 25-ml. aliquot is transferred to a 250-ml. beaker containing distilled water and a large piece of ice. The solution is titrated with standard potassium permanganate to an end point which persists for one minute.

DISCUSSION OF RESULTS

This procedure was applied to two samples of oleum which had been analyzed by the familiar nitrometer method. It was noted that the electrometric end point preceded the visual end point by 0.12 ml., which was assumed to be due to the excess ferrous sulfate that is added to obtain a detectable color change. No correction is necessary in calculating the results by the electrometric method.

The ferrous sulfate titration of nitric acid in oleum measures only the actual nitric acid content of the sample, while the nitrometer method measures the nitrosyl sulfuric acid in addition to the nitric acid. The nitrosyl sulfuric acid present is due to the oxides of nitrogen in the nitric acid reacting with the oleum. Therefore, to place the two methods on the same basis, it was necessary to determine the nitrosyl sulfuric acid content of the oleum samples and to correct the results of the ferrous sulfate titration.

Table I. Determination of Nitric Acid in Oleum

Sample No.	Sample Weight *Grams*	Volume of $FeSO_4$ *Ml.*	Actual HNO_3 %	Total HNO_3 %	HNO_3 Nitrometer %
102–70	2.765	4.57	3.52	3.53	
	6.048	9.99	3.52	3.53	
	6.950	11.53	3.54	3.55	
	8.517	14.14	3.54	3.55	
	7.272	12.06	3.54	3.55	
	7.158	11.89	3.54	3.55	
				Av. 3.54	3.57
102–71	4.837	15.36	6.73	6.74	
	3.476	11.10	6.78	6.79	
	6.071	19.41	6.77	6.78	
	5.777	18.49	6.77	6.78	
	8.145	26.03	6.77	6.78	
	5.027	16.13	6.80	6.81	
				Av. 6.78	6.78

The data in Table I show that concordant results are obtained by this method over a fairly wide range of sample sizes, and the values agree well with the values by the nitrometer method. The actual nitric acid values are those calculated directly from the titration; the total nitric acid is the sum of the actual nitric acid and the nitric acid equivalent to the nitrosyl sulfuric acid. The nitric acid equivalent to the nitrosyl sulfuric acid in both samples is 0.01%. Although the nitrosyl sulfuric acid content of these samples is not significant, samples are encountered frequently in which it is as high as 0.1 to 0.2%.

Although this method has been applied only to oleum in this investigation, it may be applied equally well to inorganic and organic nitrates (*1*, *3*).

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RECEIVED January 18, 1947.

Eighth Conference on Applied Spectroscopy

L. T. HALLETT, Associate Editor

THE Eighth Conference on Applied Spectroscopy, sponsored by the Spectroscopy Society of Pittsburgh, was held November 13, 14, and 15 at the Mellon Institute. These local conferences were started in 1940 when George Harrison presented one paper on industrial applications of spectroscopy and were expanded over the intervening years to one-day sessions of several papers dealing with emission spectroscopy, mostly applied to metallurgy. Last year a two-day session with twelve papers on emission and absorption was held, with an attendance of 200. This year it consisted of a three-day session on emission and absorption with 24 papers and an attendance of close to 300. Far from being local, this conference attracted many from outside the Pittsburgh area. The continued growth of this group is due not only to its progressive membership but also to the untiring efforts and spirit of Mary E. Warga on the staff of the Physics Department of the University of Pittsburgh.

Most of the papers presented are of interest to readers of this journal. The majority of the authors do not, at this time, plan publication, but they will be glad to give details of their papers to those who wish to write to them. In those cases where authors plan publication, the journal is mentioned in the abstract.

Emission Spectroscopy

1. A Spectrochemical Method for the Determination of Al_2O_3 in Steel. RAYMOND H. COLIN AND D. A. GARDNER, Carnegie-Illinois Steel Corp., Gary, Ind.

A chemical separation of the acid-soluble and acid-insoluble components of the steel is made. The insoluble portion which contains that part of the aluminum present in the sample as Al_2O_3 is fused and taken up in a weak acid solution. Iron is added as an internal standard. Spectrographic examination of the solution is made by means of the well-known dropping electrode, whereby fresh solution is continuously supplied to the spark gap during exposure. The chemical preparation of the samples requires 2.5 to 3 hours with 10 minutes allowed for the spectroscopic examination. The dropping electrode is slightly modified and uses a graduated reservoir to which a hollow carbon electrode is attached by means of a rubber tubing. The solution is allowed to drop at a rate of 10 to 20 drops per minute onto a pointed solid carbon electrode. The range covered is 0.500 to 0.005%. Calibration is based on synthetic standards.

2. Spectrochemical Analysis of Pig Tin. WILEY E. STEAKLEY, Weirton Steel Co., Weirton, W. Va.

This method employs the conventional internal standard principle, using a single tin line with the alloying element lines to obtain relative intensity ratios. Pin samples approximately $^7/_{32}$ inch in diameter are used as self-electrodes. An electronic spark is used for excitation and spectra are photographed with the Baird Associates 3-meter grating spectrograph on Eastman S.A. No. 1 plates. The elements and ranges determined are as follows:

	%
Lead	0.010 to 0.50
Antimony	0.015 to 0.25
Arsenic	0.005 to 0.06
Bismuth	0.002 to 0.06
Copper	0.002 to 0.05
Aluminum	0.002 to 0.008

Standard samples were prepared by dilution of a master alloy with pure tin. The master alloy was made by adding calculated amounts of the desired impurity elements to pure tin. Several methods of sampling molten tin were tried. Homogeneous and representative samples were obtained most conveniently by the use of U-shaped Pyrex tubes. A notable increase in analytical precision was found when the samples were kept cool during sparking by using massive brass block electrode holders.

3. Spectrographic Analysis of Copper-Base Alloys. ARNO TUTEUR, Duquesne Smelting Corp., Pittsburgh, Pa.

A method is presented for the analysis of copper-base alloys using a multisource unit. The range of elements determined with an accuracy of 5 to 7% was:

	%
Tin	0.08 to 2
Lead	0.05 to 0.2
Nickel	0.01 to 2
Iron	0.1 to 0.8
Aluminum	0.1 to 2
Silicon	0.005 to 0.02
Manganese	0.6 to 1
Antimony	0.07 to 0.75

4. A Calculating Board for Determining Relative Densities without the Use of a Calibration Curve. CHARLES HALE, Copperweld Steel Co., Warren, Ohio.

The straight-line portion of an emulsion calibration curve can be constructed for any wave-length region from the densitometer readings of two selected lines in that region, one of low and one of high density, provided that both readings lie within the predetermined straight-line portion of the curve. A calculating board based on this princple is described for use in steel analysis. This board requires the densitometer readings of two iron lines and one element line for each analysis, and yields results corrected for variations in emulsion contrast from one spectrum to another and from one wave-length region to another.

5. Practical Aspects of Establishing Analytical Working Curves in Spectrographic Analysis. ROBERT W. SMITH, General Motors Corp., Flint, Mich.

The following topics were discussed: The practical considerations which govern choice of instrumentation and technique for specific problems. Factors influencing choice of equipment, plates, lines, photometric procedures, etc., in the light of speed *vs.* accuracy requirements. The problem of securing and checking adequate primary and secondary standard samples. The random and systematic errors entering into the actual analysis, together with means for their evaluation. The economic factors which govern the choice of analytical method.

The author points out that in determining cost, all factors must be considered, both direct and indirect. A great deal depends on whether the sample requires a routine determination or whether special methods must be used for its analysis. Where there is a wide variety of samples and determinations, chemical analyses may prove cheaper. The General Motors Corp. has found on the average that spectrographic analysis is one sixth to one eighth the cost of chemical methods. The spectrographic method can give more information concerning trace elements than can chemical analysis. The author made a special point that analysis is a broad subject. Because this is so, spectroscopy will sometimes give only part of the answer required, and other methods must be used. In no sense, therefore, should the spectrographer feel that he is complete in his approach, and he should seek the advice of help of others working in the analytical field with different approaches.

6. The Basis of Quantitative Computation in Spectrographic Analysis. J. H. COULLIETTE, University of Chattanooga, Chattanooga, Tenn.

Innumerable experiments have shown that the intensity of the radiant energy emitted by a volume of incandescent vapor is a function of the concentration of source atoms in the vapor.

$$I = f(N)$$

The form of the function is determined by the physical conditions existing in the vapor. Then for a mixture of two kinds of atoms within the same volume of incandescent vapor the relations may be written

$$I_1 = f(N_1) \text{ and } I_2 = f(N_2)$$

where I_1 is the intensity of a given wave length emitted by the atoms N_1, and I_2 is the intensity of a second wave length emitted by the atoms N_2. By maintaining the conditions of excitation constant and varying the concentrations of the atoms, N_1 and N_2, within the vapor, it can be shown empirically that $I_1/I_2 = f(N_1/N_2)$.

If the values of the intensity ratio obtained from measurements on a series of samples of known concentrations are plotted against the concentration ratios, a calibration curve is obtained from which the concentration ratios of these two kinds of atoms for unknown samples may be determined. This constitutes the basis for the so-called "internal standard method" (*4*) of quantitative determinations, where a known concentration (N_2) of a "standard" material is added to the sample. When the sample consists of one major constituent and one or more minor constituents, it has become customary to assume that the small deviation of this major constituent from 100% is negligible, and the basic equation is taken as

$$I_1/I_2 = f(N_1\%/100\%)$$

For materials consisting of three major constituents, one constituent (N_2) may be taken as the reference element, and the relations written as

$$I_1/I_2 = f(N_1/N_2) \text{ and } I_3/I_2 = f(N_3/N_2)$$

From the curves representing these functions for a series of known samples, the values of the concentration ratios can be determined. It is then necessary to calculate the concentrations of the individual elements from these concentration-ratios. This is done by means of the solution of the equations:

$$N_1 + N_2 + N_3 = 100\%$$
$$N_1/N_2 = a$$
$$N_3/N_2 = b$$

The simultaneous algebraic solutions of these equations gives

$$N_2 = 100/(1 + a + b)$$

This method requires the simultaneous evaluation of all the elements in the sample. If all the elements are thus determined, the precision of the method depends only upon the observational errors, since no approximations are involved.

This method of computation from the concentration ratios has been applied to the analysis of aluminum ore (*1*), furnace slags of various types (*5*), stainless steel (*2*), ferrosilicon (*3*), and barium titanate ceramic materials.

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7. Stable Working Curves as an Approach to Standard Methods of Spectrographic Analysis. WILLIAM H. MAGRUM, Simonds Saw and Steel Co., Lockport, N. Y.

This paper is the result of an investigation undertaken at the Simonds Saw and Steel Co. to eliminate the so-called working curve shifts so familiar to spectrographers. This was accomplished by studying the response of various analytical line-pairs to changing source conditions. From these data the "ideal" source for these line-pairs is determined. This ideal source does not give rise to shifting working curves. There are certain definite limits of circuit parameter settings within which the analytical results are not affected even if the exposure is made under one set of parameters and the working curves under another. This permissible parameter change immediately suggests a possibility of duplicating curves from one laboratory to another, which would eventually give rise to standard methods of spectrographic analysis.

The author made a point that focus is an important factor, but more important is the accurate calibration of each emulsion. He pointed out that, if the source is properly maintained, there will be no change in working curves.

8. Some Applications of Analysis of Variance to Spectrochemical Analysis. JOSEPH GEFFNER, Weirton Steel Co., Weirton, W. Va.

The well-known statistical technique of analysis of variance (*2*) is applied to the following problems in spectrochemical analysis: testing for homogeneity, evaluating the relative contributions of fundamental causes of deviations in analyses (*3*), and estimating the increase in precision obtained by running replicate analyses (*1*). Emphasis is placed on computational procedure and on the significance of results rather than on the statistical theory.

It is fashionable nowadays to apply statistical methods to almost all forms of analysis, and the author made a plea that its application to spectrochemical analysis could yield valuable information which present-day spectrographers are not in the habit of seeking. The average spectrographer usually does not concern himself as to whether his errors are due to chance or are real. The paper cites examples from results obtained from normal analysis to illustrate the above points. The bibliography will permit the reader to gain an idea of the statistical methods employed.

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Absorption Spectroscopy

9. Prisms Versus Gratings, 1 to 6 Microns. K. B. ADAMS AND LOUISE J. PETTERSEN, Westinghouse Research Laboratories, East Pittsburgh, Pa.

The authors point out that the grating infrared instrument is usually considered expensive research equipment. The grating instrument for routine work has proved very practical, and the use of expensive calcium fluoride or lithium fluoride cells is not necessary. The price of a 7500-line grating is not great, and it was also pointed out that a combination prism and grating instrument gives flexibility not commonly found in present-day equipment.

10. Comparison of Glower and Globar Sources for Infrared Spectrometry. R. A. FRIEDEL AND A. G. SHARKEY, JR., Bureau of Mines, Pittsburgh, Pa.

A comparison of spectral energy distributions has been made between a Globar and a Nernst-type (Insulcon) glower from 1 to 15 microns with a rock salt prism spectrometer. The curves obtained illustrate the greater advantage in energy of the glower at the black body maximum and the lesser advantage at longer wave lengths. The emission maximum for the Globar lies at 2.05 microns; the maximum for the glower shifts from 1.64 to 1.61 microns for currents of 0.5 and 1.3 amperes, respectively.

11. Use of the C—H Infrared Fine Structure for the Analysis of Liquid Mixtures. ELEANOR L. SAIER, Gulf Research & Development Co., Pittsburgh, Pa.

In an infrared spectrometer equipped with a sodium chloride prism the several closely spaced absorption bands, due to the fundamental valence bond vibrations of the C—H groups, are very poorly resolved. The use of a lithium fluoride prism allows these bands to be separated and to be used for the quantitative analysis of liquid mixtures in a semiroutine manner. The differences in the fine structure are due primarily to differences in the types of atomic groupings. Consequently, the method of analysis is particularly good for mixtures containing different classes of compounds. For example, ternary mixtures containing an oxygenated compound, an aromatic, and a paraffin are analyzed quickly and with high accuracy. All data are obtained with the samples in solution in carbon tetrachloride. Systems subject to molecular complex formation such as hydrogen bonding can, therefore, be accurately analyzed and this constitutes an important advantage of the method. The scattered radiation in this region is negligible, contributing to the ease of analysis. A series of various mixtures which are conveniently and quickly analyzed was presented with data giving comparison between synthetic and observed concentrations.

12. Microwave Absorption Spectroscopy. DONALD K. COLES, Westinghouse Electric Corp., East Pittsburgh, Pa.

Recent types of apparatus used in microwave spectroscopy are described, including methods of sweeping the oscillator frequency while amplifying the detected signals by means of a high band pass amplifier, and methods of modulating the absorption lines by means of an electric field applied to the absorbing gas. Measurement of absorption line frequencies is now possible to 1 p.p.m.

Absorption spectra of different types of molecules were discussed, together with their interpretation. It appears likely that microwave absorption will have some applications as a method of gas analysis.

13. Engineering a Continuous Flow Infrared Analyzer for Plant Use.

JOHN HOVORKA, Gulf Research & Development Co., Pittsburgh, Pa.

It was desired to obtain the continuous analysis of a multicomponent gas stream for its sulfur dioxide content, which ranges from 0 to 2% sulfur dioxide. A commercially manufactured analyzer of the Pfund type (*1*), using an infrared absorption analysis method, is used. The analyzer, optical, and recording components are manufactured by Baird Associates, Inc., Cambridge, Mass. The optical tank body is filled with carbon dioxide which is present in the stream in large concentrations. The system was engineered for plant use by centralizing electrical and gas flow controls and providing these controls with optimum-condition indicators. Automatic base (zero sulfur dioxide content) registration is provided on the recorder chart by the manufacturer, but base drift, at the high thermal sensitivity, required thermostatic control of the optics. This control is provided by placing the optical components in a constant-temperature compartment. All the electrical components are in compartments through which a small air flow is maintained. This, together with glass-enclosed mercury switching, provides explosion-proofing in an atmosphere contaminated with hydrogen, where the instrument will be used. An additional convenience in operation is an electrically controlled calibration check.

All components are mounted in a standard enclosed relay rack, which may be mounted on casters for ease in servicing.

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14. High Pressure Quartz Cells for Use in Absorption Analysis.

GILBERT KIVENSON, Mellon Institute, Pittsburgh, Pa.

The fabrication of quartz cells to withstand pressures of 100 pounds per square inch or more has always been a problem. The chief difficulty has been the sealing of the windows of the quartz cells to the rest of the assembly. The authors conditioned the joints for the receipt of metal solders by first depositing a layer of platinum by evaporating a solution of platinum chloride in organic solvent on the surface in question. The cell described has been successfully used at 100 pounds per square inch for hydrocarbons normally gaseous at ordinary pressures.

15. Principals and Principles of Spectrochemical Analysis.

W. F. MEGGERS, National Bureau of Standards, Washington, D. C.

The author gave a general history of the development of spectrographic analysis in which he said that the principles have long been known, but it was left to Bunsen and Kirchoff to give it the initial application. The importance of trace elements (which wet chemical analysis could not detect) was also a springboard from which spectrochemical methods developed. The astrophysicist has used spectroscopy a far longer time because he had no other method available to him.

Meggers made a plea for spectroscopists to put more emphasis on the fundamentals of spectroscopy such as the mechanism of atomic radiation. It is only through such fundamental studies that real progress can be made in applied spectroscopy. It has been the writer's privilege to hear Meggers several times, and the present paper is outstanding in presenting principles and viewpoints which every spectrographer should know. Fortunately this paper is now in press and is tentatively scheduled for appearance in December in *Spectrochimica Acta.*

16. A Compilation of Suggested Methods of Spectrochemical Analysis.

CHARLES L. GUETTEL, Driver-Harris Co., Harrison, N. J.

The A.S.T.M. Committee E-2 on Spectrochemical Analysis has set as its immediate goal the formulation of suggested methods of analysis rather than standard methods. An outline form prepared by Subcommittee III (Editorial) for a suggested method was presented. Instructions for using the outline and an illustrative method following the prescribed form have been prepared.

Most of us know something about the work of Committee E-2 of the A.S.T.M. on spectrographic analysis. It has been struggling with the problem of standardization of methods which have not, at present, led to a very satisfactory conclusion. Because of the diversity of methods now employed and the inability of spectrographers to accept any standard method, a new approach has been suggested which would consist of a compilation of actual working methods which, it is hoped, will be useful to established laboratories as well as to beginners in the field. It is hoped also that the set of methods will eventually lead to some standardization of procedures and equipment and possibly to the adoption of standard methods. The objective of this effort seems entirely worthy, and all spectrographers are asked to consider sending to the committee on a prescribed form the methods which they now successfully employ in their own laboratories. This prescribed form may be obtained from Charles L. Guettel. However, as this is a very large subject, subcommittee chairmen have been appointed to whom the suggested methods should be sent:

Subcommittee V. Copper, Nickel and Their Alloys
P. Leichtle, Chairman, Chase Brass & Copper Co., Waterbury 91, Conn.
Subcommittee VI. Lead, Tin, Antimony, and Their Alloys
E. K. Jaycox, Chairman, Bell Telephone Laboratories, Inc., Murray Hill, N. J.
Subcommittee VII. Aluminum, Magnesium, and Their Alloys
J. R. Churchill, Chairman, Aluminum Research Laboratories, Aluminum Company of America, New Kensington, Pa.
Subcommittee VIII. Zinc, Cadmium, and Their Alloys
H. R. Youngkrantz, Chairman, Apex Smelting Co., 2537 West Taylor St., Chicago 12, Ill.
Subcommittee IX. Ferrous Metals
P. R. Irish, Chairman, Bethlehem Steel Co., Bethlehem, Pa.
Subcommittee X. Non-Metals
R. H. Bell, Chairman, Lucius Pitkin Co., Inc., 47 Fulton St., New York, N. Y.

17. Spectrophotometric and Solubility Methods for the Determination of monomer in Polystyrene.

J. J. MCGOVERN, J. M. GRIM, AND W. C. TEACH, Mellon Institute, Pittsburgh, Pa.

An ultraviolet spectrophotometric procedure has been developed for the rapid and accurate determination of monomer in polystyrene. For the same analysis, a method dependent upon the solubility of the sample in methanol has also been devised. Results of the two methods are compared. It is shown that a large reproducible difference in the answers obtained by the two procedures can be taken as an indication of the presence of an additive in the polystyrene.

18. Performance Characteristics of the Cary Recording Spectrophotometer.

R. B. HANNAN, J. H. LIEBLICH, AND A. L. MARSTON, Mellon Institute, Pittsburgh, Pa.

The Cary recording spectrophotometer (Applied Physics Corp.) will record automatically absorption spectra in the ultraviolet region from 2100 to 4000 Å. and in the visible region from 3500 to 7250 Å. Essential performance features of the instrument were described and compared with the Beckman quartz spectrophotometer, with respect to resolution, reproducibility, spectral response, wave-length calibration, and stray spectral energy. It is concluded that the instrument is invaluable for the rapid and accurate recording of absorption spectra over wide regions of the spectrum.

In summary, the author indicated that the Cary recording spectrophotometer operates well within the specifications laid down by the makers. Inherently, it has more resolution than the standard Beckman instrument, but both instruments have their place. For quick survey work, the recording model, of course, can given information quickly and present data which may form the basis of an analytical method. When the method is completely worked out, the standard model Beckman may be more suitable.

19. Steric Hindrance and Short Wave Length Bands in the Ultraviolet Spectra of Some Naphthalene and Diphenyl Derivatives.

R. A. FRIEDEL, MILTON ORCHIN, AND LESLIE REGGEL, Bureau of Mines, Pittsburgh, Pa.

Steric hindrance effects are discussed in connection with the spectra of 1,1′-, 1,2′-, and 2,2′-dinaphthyl, 1- and 2-phenylnaphthalene, diphenyl, and various derivatives of some of these compounds. Short wave-length peaks are detected in the region 205 to 212 millimicrons for compounds containing two aromatic ring systems conjugated without steric hindrance. These bands and the longer wave-length bands appear to converge toward each other when the coplanarity of the system is hindered by introduction of interfering groups.

Using a standard Beckman instrument and making corrections for scattered energy, the author extended the range so that results were obtained in the 202 to 212 millimicron region by adding a 10,000-, or better, 20,000-megohm Victoreen resistor.

20. Influence of Gases on the Spark Spectral Excitation of Aluminum Alloys. B. F. SCRIBNER, C. H. CORLISS, AND M. B. CAVANAGH, National Bureau of Standards, Washington, D. C.

The spectrochemical analysis of aluminum alloys is complicated by shifts in analytical curves as a result of major differences in composition of the alloys. These shifts have necessitated the application of a wide variety of standard samples for accurate results. The literature (*1–4*) concerning this effect was reviewed, and the results of an investigation of the effect, observed with the point-to-plane spark excitation, were presented. Observations of the spectra excited by this spark in atmospheres of air, nitrogen, helium, and carbon dioxide have shown that the effect is a function of the amount of oxygen present and may be eliminated by the application of an inert atmosphere. Studies of the spark excitation under various discharge conditions with counter electrodes of zinc, cadmium, and graphite and with the four atmospheres have shown the spark in a nitrogen atmosphere to be capable of highest accuracy. A simple apparatus for sparking disk samples in a controlled atmosphere was described.

The apparatus consisted of an ordinary Petri spark stand surrounded by a bell jar through which nitrogen flowed to maintain an atmosphere free of oxygen. It is planned to publish this paper in the *Journal of Research of the National Bureau of Standards.*

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Direct Reading Instruments (Quantometers)

21. A Direct-Reading Spectrometer for the Analysis of Steel. E. R. VANCE, Timken Roller Bearing Co., Canton, Ohio.

The first direct-reading spectrometer to be used for the analysis of steel has been installed and is in use 24 hours daily to control the product of seven electric and three open hearth furnaces.

There are approximately 150 tests on which 1300 determinations are made for each 24-hour period. Elements reported are manganese, silicon, chromium, nickel, molybdenum, copper, vanadium, and tin. One operator is used on each 8-hour turn.

Cast steel pins, $^7/_{32}$ inch, are used for analysis which are taken with the aid of a glass tube which has been sealed under vacuum. Samples are quenched in water, cut in two, and sent in a pneumatic tube to the laboratory. The pins are ground to a point on both ends in order to permit duplicate exposure; then placed in the electrode holders, and power is applied, after which the operation of the spectrometer is fully automatic. Within 40 seconds after the power is turned on, a report for eight elements is read from the calibrated clock dials and reported to the melting department.

The Dow-Baird instrument is used. The author pointed out that this instrument is being used for quick control work. However, it has not been used a sufficient length of time to rely upon it entirely for final specification work. For this they still use the chemical methods, but found that the spectrographic method in practically all cases checked the chemical procedure very closely, and it is hoped that when more data are obtained the spectrographic method may be used for final specification work.

22. Applied Quantometry in the Aluminum Industry. F. R. POTTER, Aluminum Research Laboratories, New Kensington, Pa.

Quantometry has become an integral part of production, controlling as it does the entire output of one of the largest aluminum sheet mills in the world. In seven months a single instrument (Applied Research Laboratories model) has turned out over 350,000 determinations, faster, more accurately, and more economically than the chemical or spectrographic methods previously used. Both metallurgists and production men now believe the Quantometer or its equivalent to be a necessity for efficient operation. The Quantometer has provided valuable research information and has made possible exact determinations of magnesium and silicon in the range of 0.0001%. Direct-reading spectroscopic instruments will have an increasingly important influence on the organization and production methods of metallurgical plants in the future. All large fabricating and castings plants in the aluminum industry will eventually be equipped with control equipment of this type. The major aim will be product improvement and production economy with analytical costs and instrument costs as secondary considerations.

23. Details in the Analysis of Steels with the Quantometer. M. F. HASLER, Applied Research Laboratories, Glendale, Calif.

The problem of providing the optimum in accurate, direct-reading spectrochemical analyses for the steel industry has been given further study with the Quantometer. A variety of spectrum lines for each element have been examined under several source conditions and choices made for each concentrational range. Reproducibility figures for some of the most important ranges of various elements were discussed.

The author pointed out that methods do exist, and are practical for, the analysis of steels. Proper working curves, of course, must be worked out which correct for the influence of one element on another. A typical example was cited for the analysis of chromium, nickel, and molybdenum alloys.

Naturally, spectrographers are watching with interest the application of the Quantometer to analytical problems mainly in the metallurgical field. The papers presented gave considerable data and background as to their usefulness as well as to their limitations. The elimination of photographic film with its variability is, of course, a great step forward. The correction for background is easily accomplished with these instruments. The fundamental weakness of these instruments is their lack of versatility when changing from alloy to alloy. However, considerable progress has been made in this direction, and it would seem that the establishment of working curves with standard samples solves this problem in the main. The prepared calibration strips as used with the Applied Research Laboratory model give extreme versatility with constantly changing alloys. There is no doubt that for product control the Quantometer will speed up plant operations and give a closer control of quality with less loss of spoiled melt. However, it is our feeling that these instruments will not displace chemical methods nor photographic emission instruments. These will be used more and more for special research on methods and in the establishing of working conditions for the rather expensive Quantometer. It would seem at present that a very careful analysis of analytical practice in relation to plant control must be undertaken before a Quantometer can be justified. After studying all the factors (cost, the number of alloys to be run, etc.), if the time of analysis can be considerably shortened and plant practice can be speeded up, then the installation of a Quantometer can be justified. The precision and accuracy obtained with the apparatus appear equal to, and in some cases better than, those formerly obtained by using photographic film.

BOOK REVIEW

Colorimetric Methods for Rapid Analysis of Silicate Materials. *Rune Hedin.* 110 pages. Proceedings, No. 8, Swedish Cement and Concrete Institute, Royal Institute of Technology, Stockholm, Sweden, 1947. Price, 10 kr.

This treatise describes a procedure for the determination of SiO_2, Fe_2O_3, Al_2O_3, TiO_2, CaO, MgO, Na_2O, and K_2O in a total analysis of silicate materials, with all except CaO determined colorimetrically. The colorimeter is of unique design. A mercury discharge lamp is used with filters selected to screen out individual spectral lines. Two photoelectric cells of the selenium barrier type are connected in a compensating circuit and balanced optically, by means of iris diaphragms, to secure zero deflection of a galvanometer. Comparison solutions of known concentration are not used in the determinations.

The author describes methods of preparing three sample solutions from an original sample: (1) for determination of Na_2O and K_2O; (2) for SiO_2, Fe_2O_3, Al_2O_3, and TiO_2; (3) for CaO and MgO. The reagents for colorimetric determinations in these solutions are selected for each constituent with reference to possible interference from other constituents present. Extensive experiments are reported, in which the effects of such interferences are considered, and also the effects of volume of sample solution, quantity of reagent, variations in pH, and other factors bearing upon the accuracy of the determinations. A time study, reported in detail, indicates that the total analysis can be completed in 8 hours.

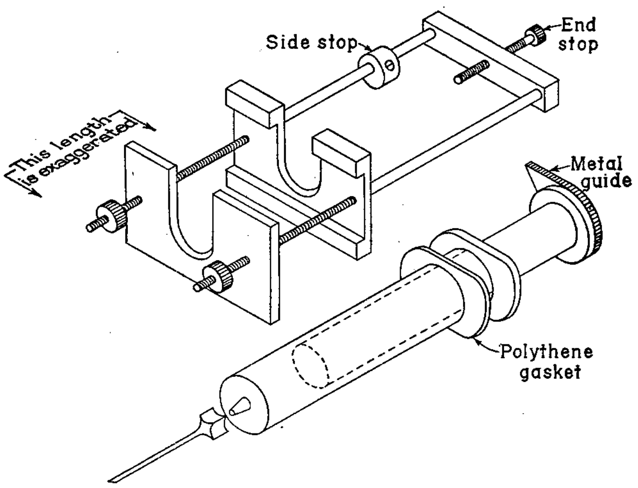
L. A. DAHL

AIDS FOR THE ANALYST . . . . .

Improved Holder for Syringe Pipets. Robert B. Dean, University of Hawaii, Honolulu, T. H. (Present address, Department of Chemistry, University of Oregon, Eugene, Ore.)

SEVERAL authors have described the use of an all-glass "hypodermic" syringe to deliver accurately known quantities of liquid. Trevor (*4*) described a micrometer buret consisting of a glass syringe driven by a machinist's micrometer. A simplified form of this apparatus has been described by the author (*1*). Krogh and Keys (*2*, *3*) described a precision pipet consisting of a glass syringe fitted with an adjustable stop.

One objection to the use of syringe volumetric apparatus has been that it is not easy to remove the syringe from its holder for washing without changing the calibration. The holder shown below was designed to overcome this difficulty. The syringe can be removed by loosening two nuts and reassembled without changing the calibration of the pipet by more than 4 parts in 10,000.



The metal holder, which is shown in an expanded form in the figure, grips the oval head of the barrel of a glass syringe, so that the top end of the barrel fits tightly against a slotted metal plate. It is this glass-to-metal contact which makes it possible to remove the syringe and replace it in the same position relative to the end stop. Greater precision might be obtained if the top of the barrel were ground flat with emery on a glass plate. The lower part of the metal clamp works through a plastic gasket to take up any uneven strain. The best gasket material is sheet polythene, such as is manufactured for lining bottle caps.

For precise work the head of the plunger must be fitted with a guide which ensures that the plunger always has the same angular orientation. A metal guide can be cemented to the plunger with Varno-Cement. A syringe fitted with a guide and a side stop can be calibrated to contain or deliver two different volumes—for example, it can be adjusted to take up 9 ml. of one solution and mix it with 1 ml. of a reagent to develop a color without exposure to the air. A microburet can be made by replacing the end stop with a machinist's micrometer.

Brass parts should be protected with a good baked lacquer such as Glyptal. A sample of polythene 0.040 inch thick was kindly supplied by E. I. du Pont de Nemours & Co. Varno-Cement is sold by the Varno Corp., 416 North Varney St., Burbank, Calif. Clear Glyptal varnish for electrical insulation is sold by the General Electric Co. and its agents. The illustration was prepared by J. Y. Nitta.

LITERATURE CITED

(1) Dean, R. B., and Fetcher, E. S., *Science*, **96**, 237 (1942).
(2) Krogh, A., Ind. Eng. Chem., Anal. Ed., **7**, 130 (1935).
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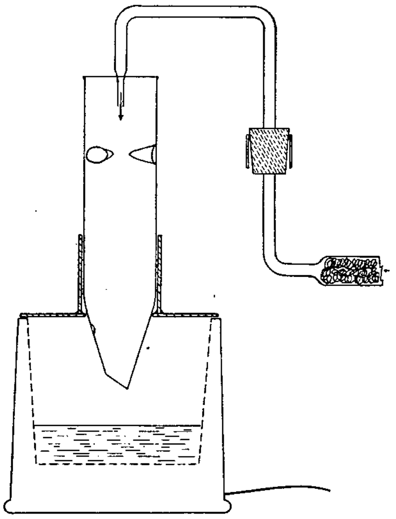
Simple Steam Microbath. Charles L. Rulfs, Purdue University, Lafayette, Ind.

THE electrolyte-solution steam microbath recently described by Marion (*4*) is similar to an assembly which the author has employed for several years, except that the author's device is a simple combination of commercially available parts. The water is heated by the electrical resistance of tap water itself. This principle has the advantages of rapidity of control and automatic cutoff.

The assembly consists of a baby bottle warmer (also marketed as an egg cooker or vaporizer) available from drugstores at less than $2 (Hankscraft Co., Madison, Wis.). A small volume of tap water will boil vigorously in this device in less than one minute. For more convenient control the user may wish to install a line cord switch. When the water is depleted, the device shuts off. Subsequent refilling is best done with distilled water to prevent the accumulation of more salts than is necessary or desirable. One may mount any desired form of head atop the boiler, but the author prefers the standard microware shown in the sketch. This consists of a 3-inch water bath ring of the type sold by micro supply houses. It is designed to hold either the glass support for microbeakers as shown, or a support for heating centrifuge cones. The filtered air blast as suggested by Benedetti-Pichler (*1*) is an invaluable accessory whenever the intended purpose is evaporation rather than mere warming.



Such a bath has proved the most convenient and simplest of many types tried, particularly in quantitative inorganic microwork where the ready availability of heating and evaporating equipment is mandatory to rapid operations. This bath can replace many of the types described by Hecht and Donau (*3*), Emich (*2*), and others.

LITERATURE CITED

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(2) Emich, F., and Schneider, F., (tr.), "Microchemical Laboratory Manual," New York, John Wiley & Sons, 1932.
(3) Hecht, F., and Donau, J., "Anorganische Mikrogewichtsanalyse," Vienna, Julius Springer, 1940 (Alien Property Custodian Reprint A-107).
(4) Marion, A. P., Ind. Eng. Chem., Anal. Ed., **18**, 82 (1946).

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Volume 19—1947

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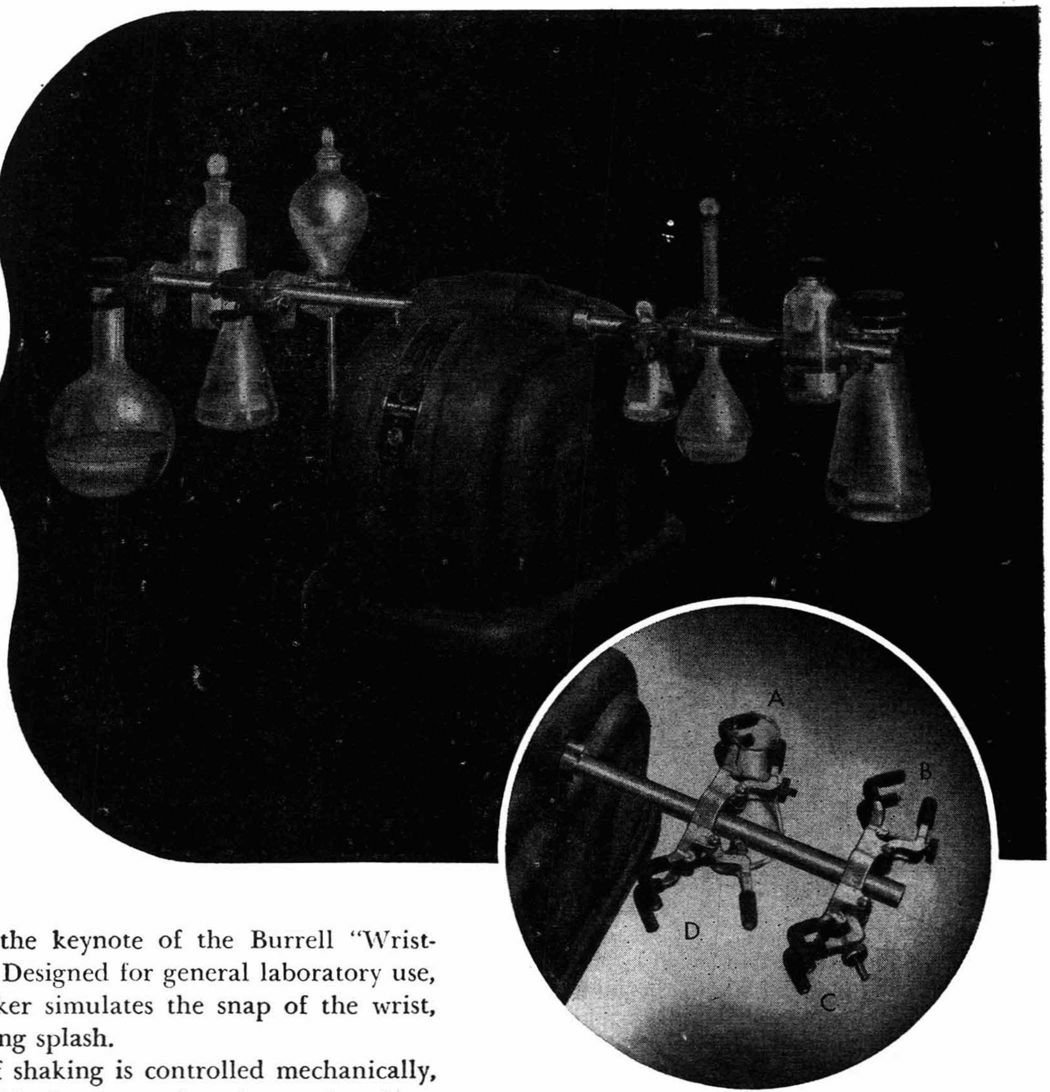

Versatility is the keynote of the Burrell "Wrist-Action" Shaker. Designed for general laboratory use, the Burrell Shaker simulates the snap of the wrist, creating a swirling splash.

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The Burrell "Wrist-Action" Shaker is furnished in three sizes—size B for eight flasks, size C for twelve flasks, and size D for sixteen flasks.

It is supplied with cord and plug for operation on 115 volt, 60 cycle current unless otherwise specified.

The spring-latch mechanism of the Finger-Grip Clamp makes insertion and removal of flasks a simple procedure. Pictured is the Finger-Grip Clamp in all of its varied positions:

A Gripping flask.
B Maximum gripping position, 55 mm.
C Minimum gripping position, 5 mm.
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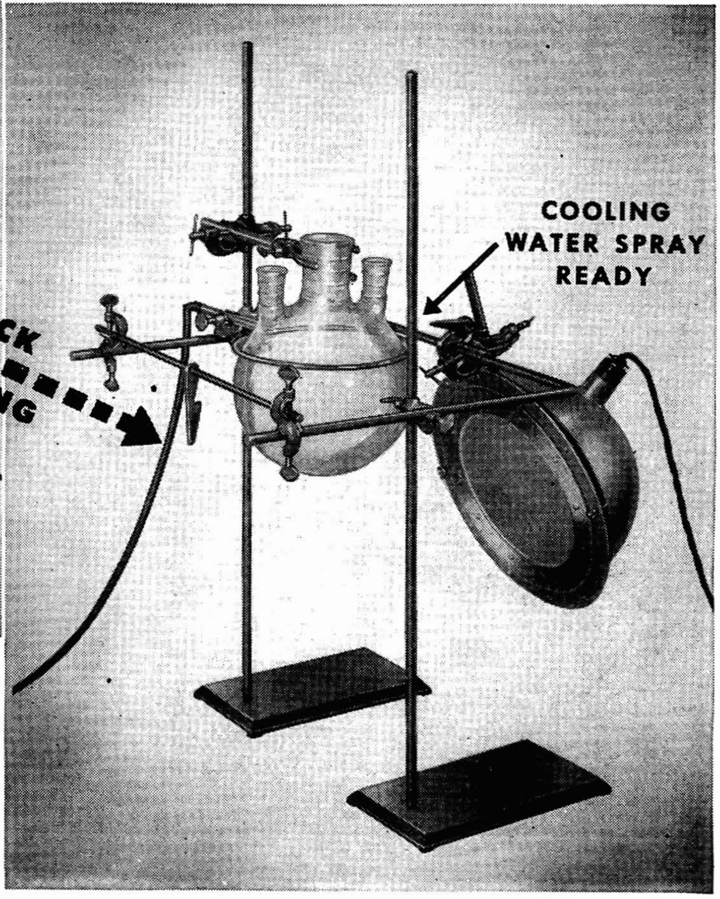
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INSTRUMENTATION

Two recently developed converter elements are described which should find extensive application in the design of instruments for the use of the analyst

by Ralph H. Müller

The search for new and improved converter elements continues unabated. Suitable means for utilizing the small d.c. potentials developed by thermocouples, thermopiles, bolometer systems, and other low impedance generators are indispensable for many of the instruments required by the analyst. We have discussed these devices from time to time and it is an encouraging mark of continued progress that once more it becomes necessary to describe a new approach.

The vibrating reed converter is now familiar. It provides for the synchronous switching of the input potential in alternate directions through the primary of a matching transformer, the output of which can be amplified to operate a servo-mechanism for indication and recording as well as the cancellation of the input signal. Among many other uses, this device is the basis of two well-known high-speed recording potentiometers—the Brown Electronik and the Leeds & Northrup Speedomax. The General Electric Autopot which we described last September uses a twin phototube to detect the deflections of a primary mirror-galvanometer and passes a definite fraction of the amplified photocurrent in opposition through the galvanometer. The feed-back current is thus an accurate and greatly magnified measure of the input signal.

Electromechanical Amplifier

The new approach is generically related to the Autopot, but it is an electromechanical equivalent. As described in the current issue of *Electronics* [**20**, 117 (1947)], the electromechanical d.c. amplifier is the instrument developed by C. G. Roper and J. F. Engelberger of Manning, Maxwell and Moore, Inc., Bridgeport, Conn. In this instrument a moving coil system actuates a metal vane that moves in the plane of two coils which form part of the tank circuit of an oscillator. A gain of 10^6 can be achieved in this way, but by appropriate feedback this is reduced to a net gain of 10^3 with a consequent improvement in stability and linearity. So far, the arrangement would seem to be a conventional use of well-known principles, but the authors have shown that with the extraordinary sensitivity which is inherent in this system it is at once possible to eliminate the disadvantage of a delicate galvanometer. They have redesigned the latter to the extent that the instrument can be used in aircraft.

A cylindrical galvanometer coil is placed in a radial field produced by an Alnico magnet. The geometrical disposition is similar to the voice coil in a loud speaker, and all turns are at right angles to the field. The coil suspension is replaced by a leaf spring bearing and the entire moving system, consisting of the coil at one end and the aluminum tuning flag at the other, has a very low moment of inertia. Displacements of the order of a few thousandths of an inch are sufficient to cause large changes in the oscillator output; therefore this modified, more rugged galvanometer can be expected to be very nearly as sensitive as its delicate laboratory counterpart.

Two circuits have been developed to measure the output. In one of those, the varying amplitude of the radio frequency output of the oscillator is rectified to supply the d.c. feed-back current. In conventional practice, this would be applied in opposition to the primary signal in the galvanometer coil. The authors have preferred to wind an additional coil, adjacent to the primary coil, through which the compensating feed-back current flows. By this means, the compensation is neatly isolated from the input. Complete temperature compensation can be achieved by shunting the feed-back coil with an appropriate resistor of zero temperature coefficient, whereby the feed-back ratio is changed to compensate for the temperature changes in the copper coils.

In a typical case where sufficient feedback has been introduced to limit the gain to 10^3, it turns out that this electromechanical amplifier maintains uniform gain for input frequencies between 0.1 and 20 cycles per second. In a specific application a 5-volt output was required from a thermocouple input of 5 millivolts. It is evident that steady state values as well as transients can be accommodated by this system. If higher frequency response is required, additional amplification can be used in order to retain sufficient feedback with corresponding stability. Gain is not limited to a factor of 1000. It is possible to extend the gain to 50,000 with stability.

For use in aircraft, a shock-mounted and weather-sealed model has been developed which occupies less than 40 cubic inches, weighs approximately 2 pounds, requires less than 5 watts' power, and is sufficiently rugged to withstand heavy vibrational and accelerative loading.

Among the many uses suggested for this device are: its substitution for delicate galvanometers in routine measuring assemblies; studies on thermocouple behavior and response; as an impedance changer; for the amplification of output in barrier layer cells and Pirani or ionization vacuum gages; as an amplifier for control equipment and servo-mechanisms; and as a preamplifier in radiometric measurements.

The Convectron

A sensitive vertical position indicator has been developed which should find many uses in the laboratory and industry. The Convectron is a Y-shaped, argon-filled tube in which a V-shaped nickel filament is mounted in the upper limbs. Electrical connections are made between the apex and free ends of the V. The nickel filament is heated by a.c. or d.c. to about 400° above ambient temperature. If the Y-tube is tilted from the vertical position, an unbalance voltage proportional to the sine of the angle is developed. On d.c. operation, the direction of inclination is indicated by the polarity of the unbalance signal; on a.c., direction is indicated by phase reversal.

INSTRUMENTATION

As the name implies, the behavior of this device depends upon convection currents set up in the gas and the distribution of the warmer and therefore less dense masses of gas will depend upon the relative position of the two limbs. An output signal of about 50 millivolts per degree of inclination is typical. Under favorable circumstances, a tilt of 1 second of arc can be detected, but at this level the system is highly dependent on supply voltage and ambient temperature. A brief description is to be found in *Electronics* [20, 190 (1947)] and although we have heard about it before, we have no definite information at this date about its manufacture or availability. This device has a response lag of about 0.1 second and from its sensitivity and simplicity would seem to find many uses in servo-mechanisms. The chemist can undoubtedly envision many uses in connection with recording balances, gas density or manometric measurements, and the like. It is interesting to note that it is also sensitive to linear or rotational acceleration but not to free fall.

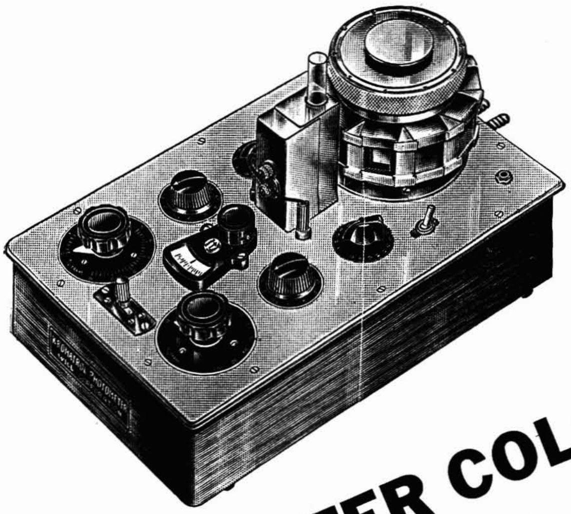
Industrial Design of Instruments

We believe that the man in the research laboratory can learn a few things from the industrial designer of instruments, best of all from the aviation industry. The average specification for aircraft instruments seems hopeless at first glance. It may require faultless performance from −50° to +120° F. to endure enormous shock and acceleration, and ridiculously narrow tolerances with respect to size, weight, and power requirements, in addition to which it should be readable by inexperienced personnel—perhaps in darkness! Nearly all physical phenomena and quite a few of chemical importance are so measured and they are not restricted to gross effects. Many delicate or minute effects such as cosmic rays or faint radar echoes are measured or recorded under such adverse circumstances.

It is therefore somewhat startling to find excessively long descriptions in our chemical journals of simple photometric or other electronic measurements in which one or two electron tubes are mounted on stone piers, surrounded by countless shields, and cooled by thermostats regulated to ±0.001° C.; perhaps the entire enclosure is pumped down to a few microns and the inevitable dishes of calcium chloride or phosphorus pentoxide stand guard over any mischievous water vapor. If there is a galvanometer at the end of this, it has a pier to itself or hangs from a Julius suspension.

We cannot avoid the impression that when an electron tube needs such solicitous care, there is something wrong with the choice of circuit. The versatility of electronic circuits is almost unlimited and great advances have been made in nonhygroscopic circuit elements as well as those with definite positive and negative temperature coefficients. The subtle distinction seems to lie in the fact that we chemists are too prone to focus attention on the electron tube and its shortcomings rather than on a good circuit in which it is only one of a number of components. From this restricted point of view our first instinct is to take over where the tube manufacturer left off, remove the base and substitute polystyrene, keep it at constant temperature and humidity, and in all respects try to make it as dependable as a Type K2 potentiometer.

The industrial designer is subjected to so many restrictions—for example, he may be limited to less than a cubic foot of space instead of a subbasement, and thermostats are out of the question. Consequently, he may be forced to use ingenuity and, as a result, discover something new. He will strive constantly for null methods, feed-back compensation, circuit arrangements which call for short-term stability and, although he may finish the race with a dozen or more tubes, the circuit itself will compensate for most of the disturbing factors.



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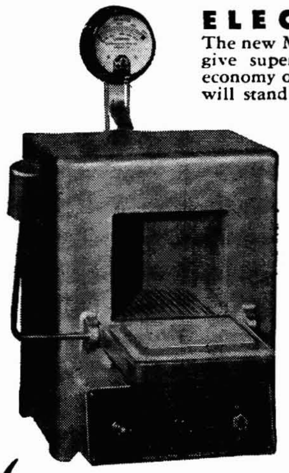

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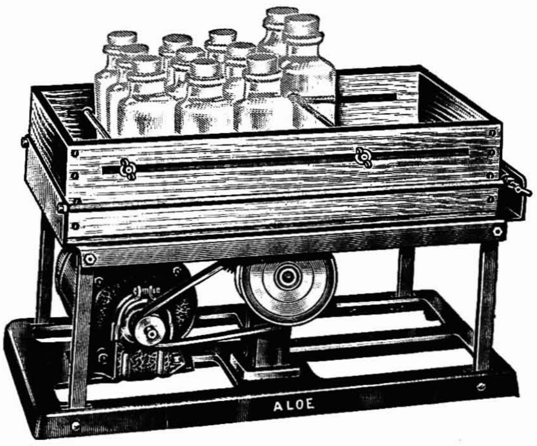

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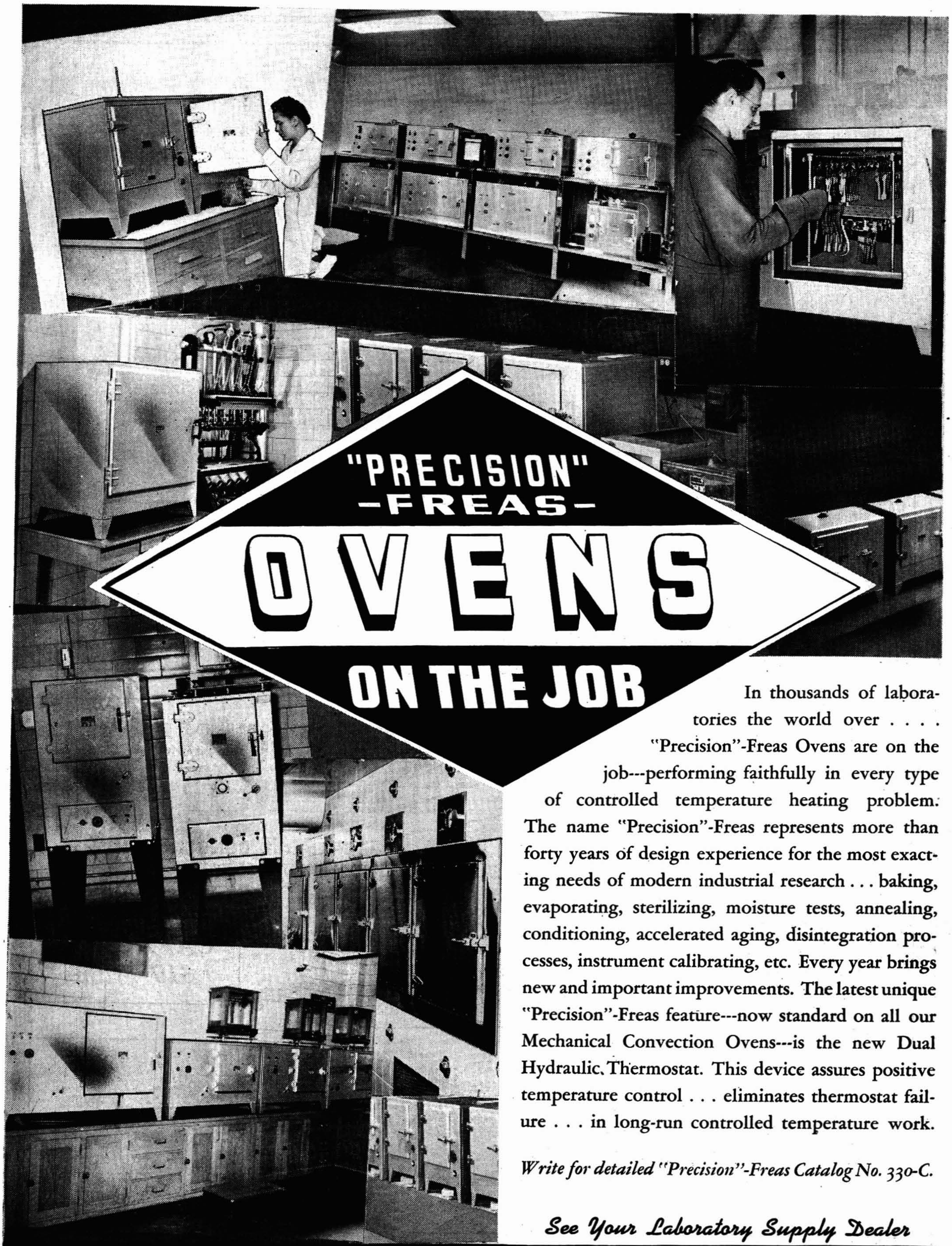

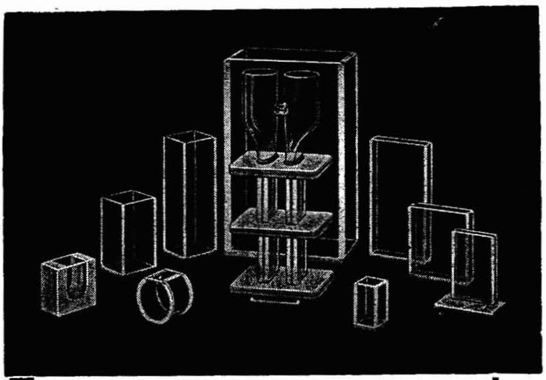

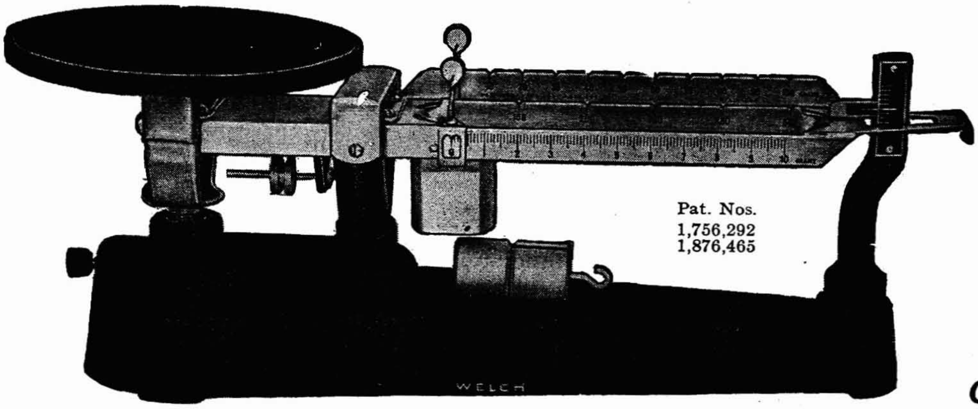
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0	—.68	—.47	—.26	—.04	—.18	.40	.62	.84	1.06	1.29	1.52
100	1.52	1.74	1.97	2.20	2.43	2.66	2.89	3.12	3.36	3.59	3.82
200	3.82	4.05	4.28	4.51	4.74	4.97	5.19	5.42	5.64	5.87	6.09
300	6.09	6.31	6.53	6.75	6.98	7.20	7.42	7.64	7.87	8.09	8.31
400	8.31	8.53	8.76	8.98	9.20	9.43	9.66	9.88	10.11	10.33	10.56
500	10.56	10.79	11.02	11.25	11.47	11.70	11.93	12.16	12.39	12.62	12.85
600	12.85	13.08	13.31	13.55	13.78	14.01	14.24	14.48	14.71	14.94	15.18
700	15.18	15.41	15.64	15.88	16.11	16.35	16.58	16.82	17.05	17.29	17.52
800	17.52	17.75	17.99	18.22	18.46	18.70	18.93	19.17	19.41	19.64	19.88
900	19.88	20.12	20.36	20.59	20.83	21.07	21.30	21.54	21.78	22.01	22.25
1000	22.25	22.49	22.72	22.96	23.20	23.43	23.67	23.91	24.14	24.38	24.62
1100	24.62	24.85	25.09	25.33	25.57	25.80	26.04	26.27	26.51	26.74	26.98
1200	26.98	27.21	27.45	27.68	27.92	28.15	28.39	28.62	28.86	29.09	29.33
1300	29.33	29.56	29.79	30.02	30.26	30.49	30.72	30.96	31.19	31.42	31.65
1400	31.65	31.88	32.11	32.34	32.57	32.80	33.03	33.26	33.49	33.71	33.94
1500	33.94	34.17	34.40	34.62	34.85	35.08	35.30	35.53	35.75	35.98	36.20
1600	36.20	36.42	36.65	36.87	37.10	37.32	37.54	37.76	37.99	38.21	38.43
1700	38.43	38.65	38.87	39.09	39.31	39.53	39.75	39.96	40.18	40.40	40.62
1800	40.62	40.83	41.05	41.27	41.48	41.70	41.91	42.13	42.34	42.56	42.77
1900	42.77	42.98	43.20	43.41	43.62	43.83	44.04	44.26	44.47	44.68	44.89
2000	44.89	45.10	45.31	45.52	45.73	45.93	46.14	46.35	46.56	46.76	46.97
2100	46.97	47.18	47.38	47.59	47.79	47.99	48.20	48.40	48.61	48.81	49.01
2200	49.01	49.21	49.41	49.61	49.81	50.01	50.21	50.41	50.61	50.80	51.00
2300	51.00	51.20	51.39	51.59	51.78	51.98	52.17	52.37	52.56	52.75	52.95
2400	52.95	53.14	53.33	53.52	53.71	53.90	54.09	54.28	54.47	54.66	54.85
2500	54.85	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

(Adopted 10-25-32)
†See Bureau of Standards Research Papers—
R.P. 767 for "Standard Tables for Chromel-Alumel Thermocouples."
R.P. 768 for "Method of Testing Thermocouples."
R.P. 1278 for "Stability of Base Metal Thermocouples in Air at 800° to 2200° F."


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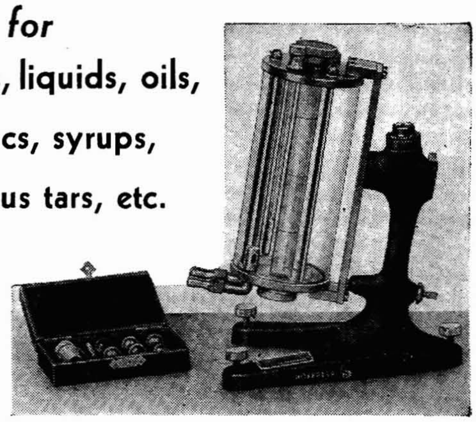

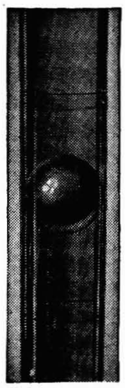

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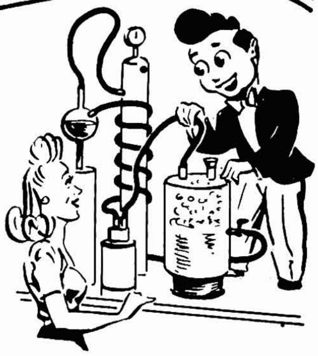

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3/16	1/16	.18	1/2	3/32	.53
1/4	1/16	.22	5/8	3/32	.65
1/4	3/16	.74	3/4	1/8	.90
5/16	1/16	.27	1	1/8	1 20

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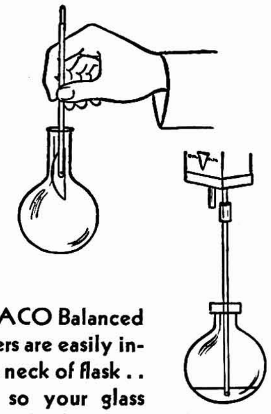

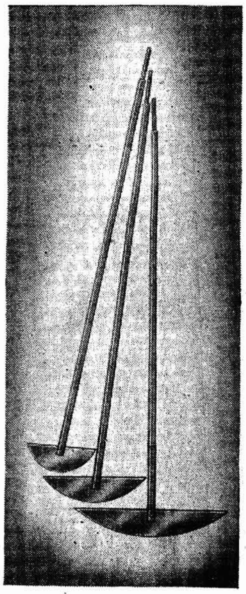

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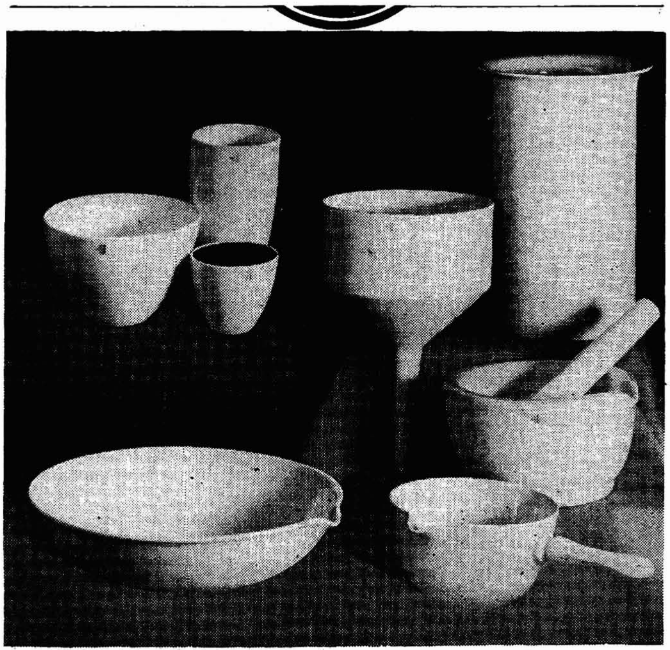

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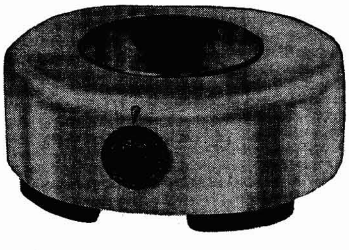

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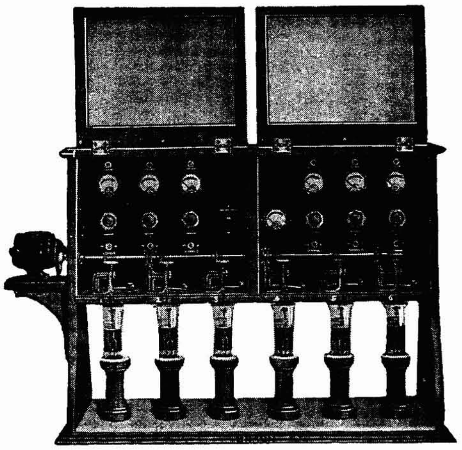

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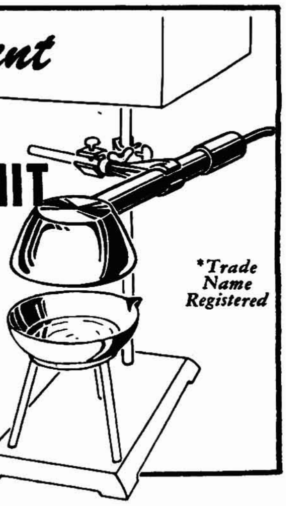

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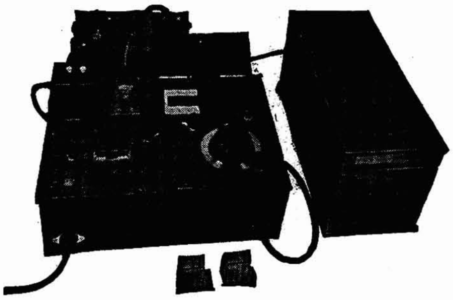

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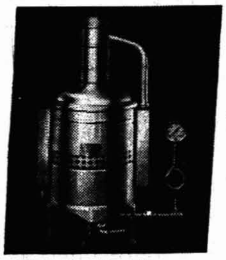

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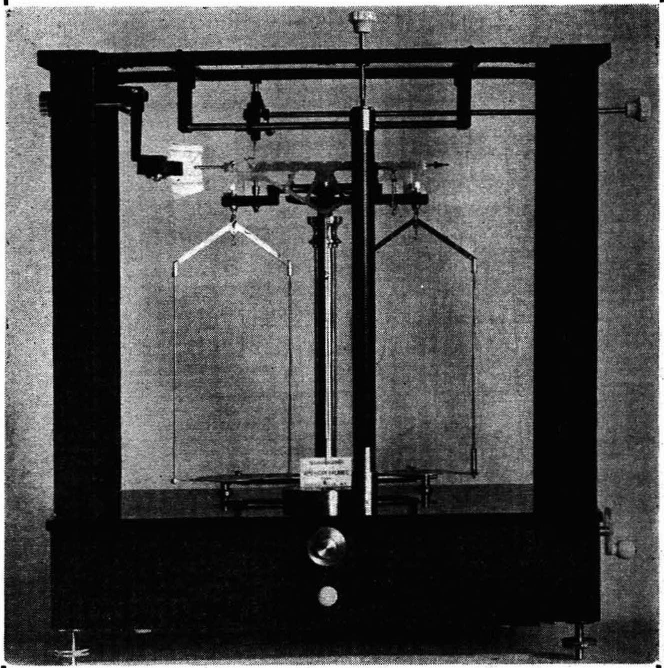

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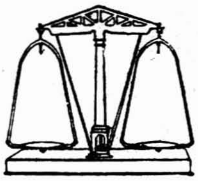

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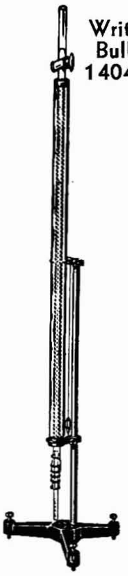

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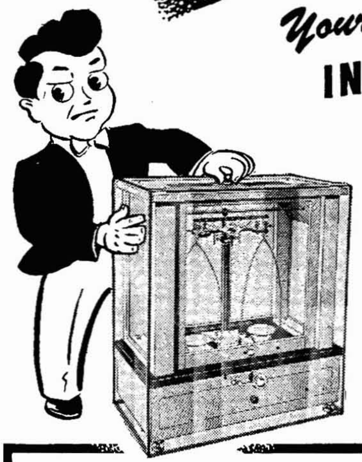

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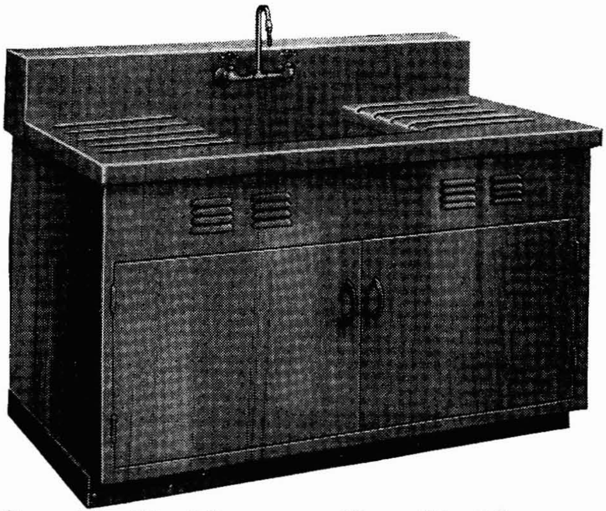

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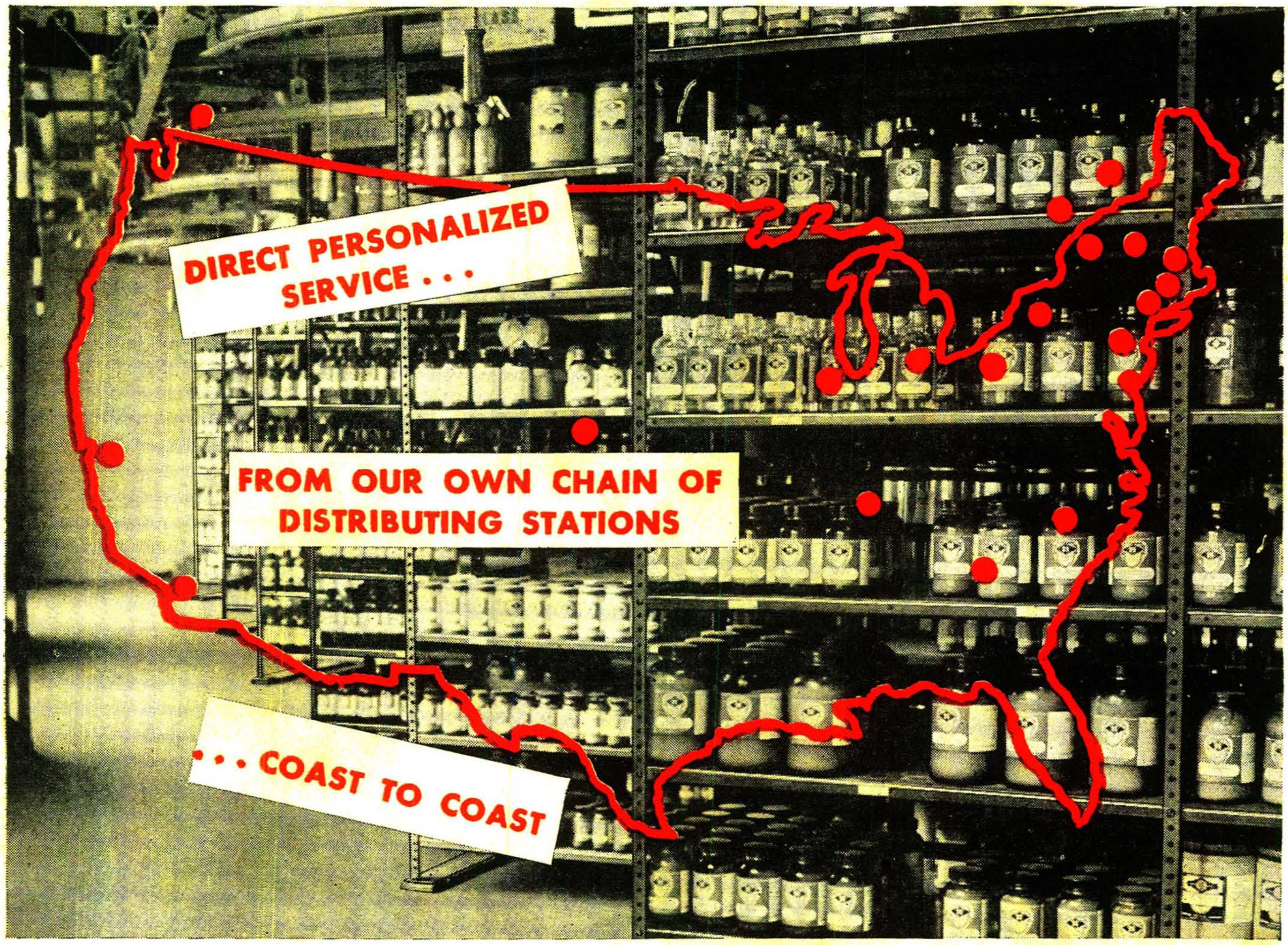
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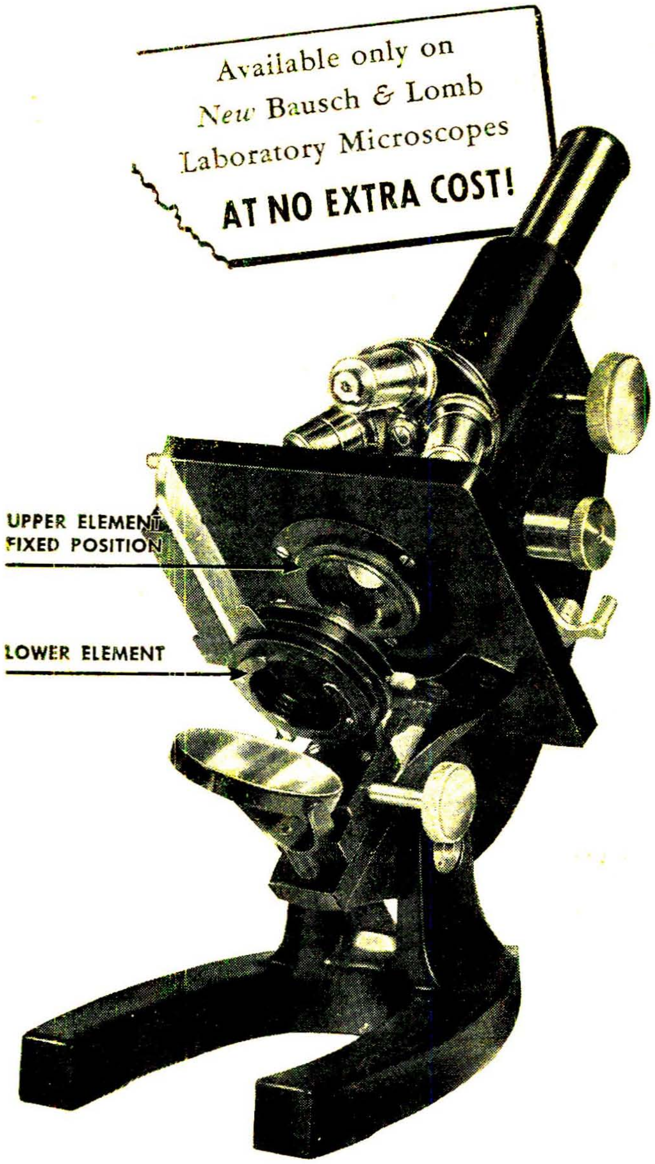
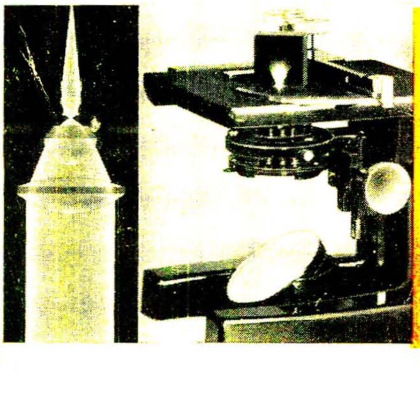
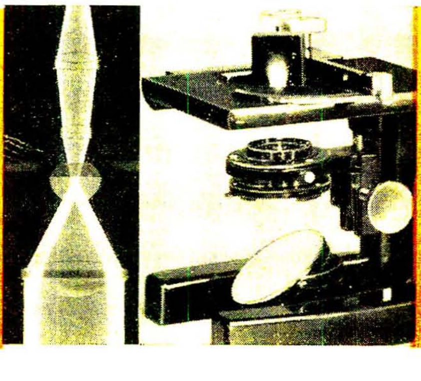


Upper and lower lenses of the B&L Variable Focus Condenser racked close together to focus illumination for the 4 mm objective. Note concentrated light cone.



Upper and lower lenses of the B&L Variable Focus Condenser separated to focus illumination for the 16 mm objective. Note the broadened cone of light.



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