Busy Months Ahead

THE Division of Analytical and Micro Chemistry and ANALYTICAL CHEMISTRY will cosponsor a Symposium on Analytical Methods in Nuclear Chemistry, to be held at Northwestern University, Evanston, Ill., Friday and Saturday, August 13 and 14. The officers of the division and the editors of this publication intend that a summer symposium shall be held each year. Such affairs will provide ample opportunity to cover some one subject of great importance in the field of analytical chemistry in greater detail than is possible at the regular sessions of the division held during the national meetings of the Society.

The subject selected for the initial symposium is one of such special significance that we feel that it is unnecessary to sell it to the analytical chemists. Through the fine generosity of R. K. Summerbell, head of the Chemistry Department at Northwestern Technological Institute, the excellent facilities at Evanston will be made available to us, including a limited amount of dormitory space. Under the able direction of Philip J. Elving, chairman of the division, a number of committees are hard at work arranging the program. We anticipate a heavy attendance and earnestly suggest that those who wish to attend signify their intention to do so as soon as the complete details are announced, as they will be in both *Chemical and Engineering News* and ANALYTICAL CHEMISTRY.

It is obvious that analytical chemists are in for a busy summer period, for we also are privileged to announce that under the auspices of the Netherlands Chemical Society an international congress on analytical chemistry will be held at Utrecht, Holland, on June 1, 2, and 3. The organizing committee is headed by C. J. van Nieuwenburg, with H. A. J. Pieters as secretary. The three-day session will be divided into five sections, as follows:

1. General Methods; Standardization
2. Electrical Methods
3. Emission Spectrography
4. Optical Methods; Chromatography
5. Microbiological Methods and Traces

Further details are published on page 185 of this issue.

It is a happy augury to us that on both sides of the Atlantic special meetings of analytical chemists will be held this coming summer, indicating a strong resurgence of interest in the field of analytical chemistry. We hope that a number of British and European analysts will find it possible to be with us in August and also that a representative delegation of American analytical chemists will be in attendance at Utrecht in June. Such gatherings at international meetings will advance the science rapidly and will help to lay the groundwork for close cooperation within the various commissions of the International Union which have to do with matters of analytical chemistry. We think it unnecessary to elaborate in detail on the desirability of international agreement. Standardization in many directions is badly needed and long overdue. There is nothing like frequent personal contact to bring about a meeting of minds. Correspondence often has just the opposite effect.

SYMPOSIUM ON PURITY AND IDENTITY OF ORGANIC COMPOUNDS

Introductory Remarks

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IN THE early days of modern chemistry, practically all chemistry was analytical. In their quest for more knowledge concerning the composition of the world in which they lived, investigators devoted their time exclusively to the task of breaking down or analyzing naturally occurring materials. Upon these researches was founded the science of analytical chemistry which has flourished for centuries and which continued up into the 19th century to command the attention of the great majority of chemists. With the laboratory synthesis of the first organic compound, however, there began a new era—the age of synthetic organic chemistry. This change brought with it a never-ending expansion of the over-all complexity of the science of chemistry, and in contrast with the earlier times, greater emphasis in recent years has been placed upon the building up of more complicated structures than upon the tearing down of the more simple of the natural products. So complete was the swing of the pendulum that the science of analytical chemistry suffered greatly from lack of attention. Only in certain schools, and in the research laboratories of a limited number of individual scientists, did the analyst receive the recognition he deserved; only in these isolated places was outstanding research done to advance the science of analysis.

Fortunately, the pendulum has begun to return to a more normal position, and once again the analyst is beginning to come into his own. The complex nature of the products of today and the multiplicity and types of uses to which they are being put have of necessity focused a great deal of attention upon the value and importance of critical analyses. No longer does a determination of such constants as refractive index or melting or boiling points, or even a carbon-hydrogen-nitrogen analysis satisfy the organic chemist. Both in the field of production control and in fundamental research, there is an increasing demand for analytical data which go far beyond those mentioned above. Consequently, today, scientists in larger numbers are again being attracted to the field of analysis; strong research groups are being organized to study analytical procedures; much progress is being made. Results and determinations, of an accuracy and a nature until recently thought to be unobtainable, are now commonplace, and still the search for better methods and instruments must go on.

INSTRUMENTAL ANALYSIS

With high premiums placed upon accuracy, specificity, and the speed with which results can be obtained, the analyst has called frequently upon the physicist and the instrument maker for assistance and cooperation, and out of this union has come a new branch of analysis—instrumental analysis. Academic curricula have been modified to enable the analytical chemist to study more physics, and to devote more time to the experimental use of scientific instruments. Today Ph.D. degrees in chemistry are awarded in instrumental analysis. The realization that "cutting wood with a hammer" is at best an inefficient process

has led to a widespread appreciation of a more complete instrumentation both in the laboratory and in the plant.

The expression "instrumental analysis" is intended to include those methods of analysis which are performed essentially through the use of instruments, and which are performed upon the substance itself and not upon any reaction product thereof. In general, it may be said that these analyses depend upon the determination of some physical constant or constants of the sample or upon its physical behavior rather than its chemical reactivity. It is the goal of the analyst to select a physical constant which lends itself to direct measurement and which itself characterizes the material or the phenomenon being analyzed. Wherever possible, the measurements themselves should furnish the desired information and thus eliminate the necessity for obtaining this information by deductive reasoning.

In addition to the advantage of directness and specificity, the methods of the instrumentalist more often than not lead to values both of analytical accuracy and of speed greater than those obtainable by other means. Too often, conventional methods lead to results which must be considered as "post mortems"—for they are after this need for them has passed. Innumerable instances might be cited where critical research projects have failed entirely or have been seriously delayed by the lack of sufficient analytical data when needed; where the time required for the successful transition of a laboratory process into one suitable for the plant has been made unnecessarily long and unduly expensive by the lack of analyses; where both the quality and the quantity of the final product have been low because of the lack of a suitable analytical yardstick with which to check the process at each of its stages. Analytical bottlenecks like these can frequently be broken by the use of the proper instruments; such is the task which lies ahead of the instrumental analyst.

Frequently it is argued that the proper instruments are too expensive, and in certain cases this may well be true. In general, however, this criticism is not justified. To arrive at a proper estimation of the value of a given instrument many things must be considered. A spectrophotometer for the visible spectrum was purchased early in 1937 at a cost of $7000. At a total cost of approximately $1250 for operation and upkeep it is still in daily operation eleven years later. During one year, two analysts, using this instrument, performed upwards of 14,000 quantitative determinations, ranging all the way from the measurement of the exact color of plastics, paper, textiles, paints, and leather, to the quantitative analysis of metals such as copper, phosphorus, iron, mercury, etc., and to the determination of the quantity of various sulfa drugs present in the blood and urine of experimental animals. This one instrument performed a fair percentage of the analyses required by several research groups. In determining the over-all value of this spectrophotometer, one must consider not only the tangible items such as the man-hours and the reagent costs saved, but also several very important in-

tangibles. Among these would be included the saving in laboratory space and the speed with which the research projects could be carried on, as well as the very important fact that the leaders of these research groups were able to plan their work on a much broader scale, knowing that their men would not be held up for lack of analytical help. When properly evaluated, the cost of an instrument is generally not prohibitive.

It would be out of place to attempt to discuss or even to list at this time all of the instruments which might be found in use in a modern analytical laboratory. Suffice it to say that important analytical methods have been based upon the following instruments or physical properties: polarographs, turbidimeters, electrical properties, supersonics and sonics, optical and electron microscopes, x-ray and electron diffraction, emission spectrometers, infrared, visible ultraviolet, and Raman spectrometers, microwave absorption refractometers, tracer analysis, partition chromatography, differential solubility, and fluorescence.

A recent survey entitled "Trends in Quantitative Analysis" (1) revealed the fact that over 56% of all the research papers published on quantitative analysis during the year 1946 were on instrumental methods; the number published on colorimetric methods alone was almost as great as the number on titrimetry (volumetric analysis). Thus much has been written about instrumental analysis and many symposia have been held at which the details of the individual methods have been discussed.

THE FUTURE OF ANALYSIS

What is the future of analysis? What does the future hold for the analyst? In this general connection it was proposed that a symposium be held at which the accent should be placed upon the analytical results obtained and not upon the instruments or methods used. It was intended that the discussions be concerned more specifically with the philosophy and meaning of analysis than with the tools at the disposal of the analyst.

During the preliminary study, it became apparent that practically all the problems of an organic nature which are submitted to the analyst may be placed in one of three groups: (1) the determination of purity; (2) the establishment of identity; and (3) the determination of and proof of structure. It was realized that the concepts indicated by purity, identity, and structure might well serve as the bases for three separate symposia. However, inasmuch as the first two are so closely related, it was decided to treat them simultaneously, leaving for another time the subject of structure.

Let us consider for a moment the source of the broad implications of the two concepts purity and identity as applied to analysis. Under certain conditions an unknown may be said to have been analyzed qualitatively when identity has been established between it and some known. Quantitative analysis, by analogy, may be regarded as the establishment of identity between the unknown and a plurality of knowns mixed in some fixed proportion. These facts, which are too often taken lightly, are predicated upon two assumptions—assumptions which in themselves will bear considerable study. They assume that the analyst has at his disposal a satisfactory method or methods for establishing identity between two samples, A and B; they presuppose, too, that some suitable method had previously been used to guarantee the purity of B, the known standard. To what extent are these assumptions valid? Do such methods actually exist? Just how far in this direction is one justified in attempting to go? How accurate can analytical results be?

Webster's unabridged dictionary defines purity as "freedom from foreign admixture or deleterious matter"; identity as (a) "sameness of essential character," (b) "sameness in all that constitutes the objective reality of a thing; selfsameness, oneness."

PURITY

From a theoretical point of view it is obvious that we cannot achieve absolute purity; we cannot prepare a standard sample in which every single molecule is exactly like every other molecule. The purity of a sample then must be considered as a relative rather than an absolute property. The degree of purity desired or required in a given sample varies widely, depending upon the nature of the sample and the ultimate uses for which it is intended. Thus, we fully appreciate that the word "pure" has an entirely different meaning when applied to a polymer from that which it has when used in describing a drug, an analytical reagent, or a metal; and we are seldom confused by these differences in meaning. To describe different degrees of purity, many descriptive terms are in common use. Thus a sample may be labeled as being of technical grade, practical grade, reagent grade, or chemically pure (c.p.); it may otherwise be marked to indicate that it has met the specifications of the A.C.S. Committee on Analytical Reagents, of the United States Pharmacopoeia (U.S.P.), or of the National Formulary (N.F.). The use of such qualifying terms is a great convenience in describing the quality of materials produced or purchased, but what of the validity of the analyses which are implied by these terms? What course is open to the analyst who is asked to certify whether a newly synthesized material or a fraction isolated from a natural source is pure?

One need only consider among other things the dramatic effects produced by fractional parts per million in the fields of chemotherapy, insecticides, catalysis, nutrition, and antibiotics, in order to appreciate the importance of traces. Never before has there been a greater need for knowing the exact composition or purity of the materials with which we work. To the extent practical, just as many evidences of the degree of purity of our standards should be obtained as is possible. Certainly one must not be guilty of saying or believing that a given product is pure merely "because it has a sharp melting point," or "because it has been recrystallized."

IDENTITY

A little thought is sufficient to convince us that we cannot prove that sample A is in every respect identical to sample B, for this in effect would require proving that every molecule of A is exactly like every molecule of B. We cannot therefore hope to obtain analyses of 100% accuracy, and all results must be presented and accepted as relative. Even the best of results may be interpreted as showing only that with a high degree of probability the facts deduced from them are true. One of the primary purposes of this symposium should be to call attention to those approaches to analysis which may be expected to lead to deductions having the highest possible chance of being correct.

We cannot achieve absolute purity; nor can we establish absolute identity. We can, however, consider the true meanings of these concepts as applied to the various branches of science and recognize the experimental limitations with which the analyst is faced.

Perhaps no better illustration of the importance of the above may be had than a brief reference to some phases of the recent research on penicillin. It is now well established that there are at least five different penicillins which may be produced by the conventional fermentation process. Thus any given batch of fermentation penicillin may be an unknown mixture of types. There is also evidence to show that even today no one of these types has been isolated as a pure product. Countless researches have been conducted using these impure materials—many supposed facts have been enunciated. These have dealt with chemical characterization, attempts to establish structure, the setting up of qualitative and quantitative analytical methods, and the specific therapeutic effects of the penicillin types as drugs. Many times the results obtained by different observers failed to agree. Many times, no doubt, the difficulty lay in the failure of the observers to use samples which were sufficiently identical one with the other. Finally, one of the types of penicillin was synthesized,

and to verify this it immediately became necessary to establish beyond a reasonable doubt that the natural and the synthetic products were identical. No one method was available by which this could be done, nor was any single instrument capable of furnishing as proof of identity experimental data which could not be questioned to some degree. As a result of the fact that almost complete agreement was found between the analytical values obtained from the two materials through the combined use of an impressive list of chemical, biological, and physical methods, it is possible to state that this one type of penicillin had been isolated in a relatively high state of purity and that the synthetic and the natural products were identical with a high degree of probability.

In the above example, and in dozens of other cases which might be cited, the usefulness of the various instrumental methods cannot be overemphasized. Nor can too much stress be placed upon the need which still exists for the development of analytical methods possessing an even greater power of discrimination, methods which will increase still further the probability that our results are correct.

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Philosophy of the Purity and Identity of Organic Compounds

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If a molecular system cannot be fractionated, it should be regarded as a pure system; this is the definition of a component in the thermodynamic sense of the phase rule. In cases of metastability, the length of waiting for equilibrium is determined by the experiment to be performed, and it is concluded that a system is pure for a particular purpose, if further fractionation would not yield products whose use would change the result of the experiment.

ONE might adopt an abstract definition of purity such as "a pure compound is one in which all molecules are identical." A meaning still must be given to "identical molecules." From the third law of thermodynamics, the entropy of a pure crystalline solid at the absolute zero can be taken as zero. This is equivalent to saying that under these conditions, all the molecules are in identically the same state—i.e., the molecules are all identically alike. However, at all realizable temperatures the molecules exist in different energy states; so that under ordinary conditions one must give up any idea of such complete identity. Thus we turn to a definition of purity in terms of operations to be performed. A system of molecules is a pure compound if an exhaustive series of fractionations fails to produce fractions with different properties.

What one calls a pure compound thus changes as new methods become available for separating material into fractions, or for more accurately measuring the properties of the fractions.

The usual "pure" hydrocarbons still have about every five-thousandth hydrogen atom twice as heavy as the rest and have a small amount of carbon 13. Whether it is proper to regard such a system as "pure" depends entirely on the use to be made of it. If further purification would have changed the measured properties, it was not pure, and conversely.

Thus, we arrive at a standard of purity which varies with the use to be made of the material. This lack of an absolute standard of purity may seem unsatisfactory, but it is unavoidable if purity is to mean anything but an unattainable abstraction. It is an unusual organic molecule which does not have more than one conformation. The boat and chair form of six-membered rings is an example. If the activation energy for a molecule to change from one configuration to another is 25 kg.-cal., then one can separate the isomers, and they will be stable for a matter of days at room temperature. When the activation energy is half as large, the same stability will be obtained only below 150° K.— i.e., at half room temperature on the absolute scale.

It is thus a matter of considerable interest to consider types of isomers which coexist in systems frequently considered to be pure compounds.

NUCLEAR SPIN ISOMERS

Ortho- and para-hydrogen are well known and change into each other only in the presence of paramagnetic molecules such as oxygen, paramagnetic ions such as Ni^{++} or in reactions in which the atoms of a hydrogen molecule gain new partners. In para-hydrogen, the molecules' nuclear spins are antiparallel, and the molecule can exist only in even rotational states; whereas the ortho-hydrogen has the nuclear spins parallel and can exist only in odd states. At very low temperatures only para-hydrogen in the zeroth rotational state is stable, so that in the presence of a catalyst such as charcoal, ortho-hydrogen changes over into para-hydrogen. If it is removed from the catalyst while still cold, it then can be kept at ordinary temperatures indefinitely.

More generally, any symmetrical molecule which has a number of indistinguishable orientations, σ, in space which go over into each other by rotations is said to have a symmetry number σ. Thus, hydrogen has two indistinguishable configurations, and the rotational states break up into two classes—the odd and the even state. The odd rotational states of ortho-hydrogen correspond to triplet states, and the even rotational states of para-hydrogen correspond to singlet states for nuclear spin.

In methane, there are twelve ways of orienting the molecule which are indistinguishable, so that the symmetry number σ is twelve and the rotational states break up into twelve sets. However, only three of the twelve possible sets of states are allowed for methane. In one of the allowed sets, the hydrogen nuclear spins add up to make a quintet state (4). In a second of the allowed sets, the hydrogen nuclear spins add up to make a triplet state in three different ways; and finally, in the third allowed set of rotational states, the spins add up to make a singlet in two ways. Thus, the first set of rotational states with quintet spin is fivefold degenerate due to spin; the second set is $3 \times 3 =$ ninefold degenerate due to spin; and the third set is twofold degenerate.

Actually then, a sample of methane consists of a mixture of three nuclear spin isomers which in the absence of paramagnetic molecules may not change over into each other during the lifetime of the molecule. According to MacDougall's calculations (2), the three isomers have different specific heats below 80° K.; and if a suitable catalyst could be discovered in this low temperature range, mixtures other than the metastable 5:9:2 mixture should be realized. Similar considerations apply to the possibilities of measurable separation for other molecules with sufficiently low moments of inertia, such as water and ammonia. However, all symmetrical molecules (unless the identical atoms interchanged by rotation have no nuclear spin) consist of such mixtures of stable nuclear spin isomers, whether or not you can devise experiments to isolate the isomers. It is the fashion to forget about such complications, with respect to purity, on the theory that "what the eye doesn't see, the heart doesn't grieve." This is of course the only practical procedure. To say that no procedure exists for separating isomers into fractions is to say that no error is made by treating the mixture as a pure compound, and we may anticipate a continuance of the general policy of ignoring nuclear spin isomers in organic chemistry.

ISOTOPIC MIXTURES

Besides the molecular differences associated with nuclear spins, we have molecules differing only in the number of neutrons within particular atomic nuclei. How little the naturally occurring concentrations of heavy hydrogen affect the chemical and physical properties of compounds is proved by the lateness of its discovery. In the case of deuterium, however, this is because of its low concentration (about 1 part of deuterium to 5000 of light hydrogen). The general theory of how replacing one isotope in a molecule by another modifies its properties is well understood. The potential energy curves for bonds are substantially unchanged by an isotopic interchange. However, the heavier masses vibrate more slowly. This makes them have a lower zero point energy, and so a higher activation or dissociation energy. Thus, the heavier isotopes react slightly more sluggishly than the lighter ones. In the equation for specific reaction rates

$$k' = \kappa \frac{kT}{h} e^{-\frac{\Delta F^*}{RT}}$$

it amounts to saying that the free energy of activation, ΔF^*, is in general less for reactions involving light hydrogen than for heavy hydrogen. In some reactions, such as the inversion of ammonia, there is an additional chemical inertia associated with the fact that the transmission coefficient, κ, for ND_3 for example, is less than for ammonia.

When radioactive isotopes are used, the resulting radioactive molecules are readily identified without it necessarily being easy to separate the molecules carrying the different isotopes. With respect to mixtures of isotopes, the practical philosophy again holds that "what you don't know doesn't hurt you." An isotopic impurity that can be removed only with the greatest difficulty obviously does not materially affect the results obtained when it is left in.

OPTICALLY ACTIVE ISOMERS

Any molecule which has neither a plane nor a center of symmetry is optically active and rotates plane polarized light either clockwise or counterclockwise. Ordinary methods of preparation yield the two isomers in equal amounts. Hydrogen peroxide, for example, has the two types of isomers. Thus, if we consider the plane passing through the two oxygen atoms and one of the hydrogens, the remaining oxygen-hydrogen bond lies normal to this plane in one direction or the other. These two optical isomers cannot be resolved into the pure components at room temperature only because the activation free energy for the transition from

one to the other is less than about 25,000. If the activation free energy is the nth part of this, resolution will be possible at $\frac{300}{n}$ degrees absolute. At temperatures too high to permit resolution, the mixed system is regarded as a pure compound. Below this temperature, one isomer is considered an impurity in the other. In other words, if it is experimentally possible to separate the isomers, then one isotopic is thought of as a contaminant for the other; otherwise not.

The methods of preparing optically active compounds break into two main classes. (1) The pure isomers may have a lower free energy than the mixture and so separation on standing occurs spontaneously. This happens sometimes in the crystallization of a racemic mixture or in the crystallization of a racemic mixture to which an optically active isomer of some other compound has been added. (2) The second method is the carrying through of an optically active synthesis by using a catalyst which is optically active. In this case, the free energy of activation for formation of that isomer which preferentially appears is less than for the other isomer. Since both of a pair of optical isomers possess the same primary bonds, the preferential formation of one must arise entirely from a better fitting on the catalyst of the favored activated complex. This arises because of the formation of better secondary bonds. It is of interest that the living world with its overwhelming preponderance of the levo-protein molecules indicates that all protein molecules arose from a single first pattern and that when a Walden inversion inverts a catalyst pattern, the organism carrying it is unable longer to compete and is so headed for extinction (1).

Actually, there are many types of unsymmetrical molecules, such as peroxides, which change so readily into their mirror images that they cannot be separated, and the mixture is called a pure compound.

KETO ENOL ISOMERISM

Perhaps no example of tricky isomerization is more familiar to organic chemists than the keto enol variety. Thus, if great care is taken to avoid all contamination with alkali, such as substituting quartz for ordinary glass vessels, it is possible to slow down keto enol isomerization and so make it possible to separate acetoacetic ester into ketol and enol forms. This illustrates an interesting paradox. Thus, when acetoacetic ester is in a glass vessel with a trace of alkali impurity present, it should be thought of as a pure compound; while if greater precaution is taken to avoid contamination, and it is placed in a quartz vessel, it becomes an impure mixture. In the same way, hydrogen in a vessel with a trace of catalytically active charcoal present should be thought of and in fact behaves as a pure compound; while without the contaminating charcoal, it is in fact a mixture of two compounds—ortho- and para-hydrogen.

In the case of other compounds such as acetone, although it may be difficult to separate ketol and enol forms, still our knowledge of reaction rates suggests that the power of halogen to substitute for the hydrogen proves the presence of the enol form.

PURIFICATION

Methods of purification, in general, can be broken up into equilibrium and, secondly, rate methods as was true for optical isomers. Spontaneous separation of any two compounds means simply that the resolved system has a lower free energy than the mixture. Similarly, preferential formation in reaction of one of two competing compounds means lower free energy of activation for the favored compound. Thus, in crystallization, a molecule or ion which is too large or too small to fit into the lattice of a second compound will have an improbability of entering any position in the lattice given by the expression $e - \frac{\delta F}{RT}$, where δF is the difference between the free energy change of transfer-

ring a mole of the impurity from the mother liquor to the lattice, to which it does not belong, over the same value for the lattice molecules. If the impurity is too small by one nth of the lattice position, then δF will be roughly one nth the heat of vaporization of the lattice molecule. Molecules crystallizing around room temperature often have heats of vaporization in the neighborhood of 10,000 calories. If the impurity is 25% smaller than the lattice molecule, this would make $\delta F = 2500$ calories and

$$e - \frac{\delta F}{RT} = \frac{1}{100}.$$

This shows how efficiently crystallization sorts out molecules according to size. If the impurity is too large, by the same amount, for the lattice position, its probability of entrance is even very much less because of the great energy of repulsion between molecules, so that the impurity tends to occupy wastefully more than one lattice position. Even when molecules are the same size, differences in shape may lead to large values of δF, again preventing the formation of mixed crystals. This is exemplified by the frequent failure of optical isomers to form mixed crystals. However, the optical isomers of camphor form mixed crystals in all proportions with a melting point not depending on composition. This means that the optically active part of the molecule is sufficiently buried in the molecule's interior not greatly to influence the molecule's external shape. Another evidence that the optically active part of the camphor molecule is not exposed, is found in the fact that vapor and liquid have the same optical rotation.

IDENTIFICATION

Every quantitative measurement of a physical or chemical property of a compound helps in its identification. However, the regular procedures of classification according to solubility, reactivity, and the physical properties of the compounds or of their derivatives have been remarkably successful. A structural formula is frequently referred to as being only a summary of the reactions the compound will undergo. Although this is true in part, the fact is that all the physical methods such as x-ray analysis, light absorption, etc., bear out in a startling way the deductions from type reactions, so that taken together, the evidence for structural formulas becomes overwhelming. This is apart from some of the no longer acceptable explanations of how reactions take place which have appeared in the papers of many chemists. Such theories, happily, are becoming less common.

Summarizing, we are led to conclude that if a molecular system cannot be fractionated, it should be regarded as a pure system. This is, of course, the definition of a component in the thermodynamic sense of the phase rule, as Webb points out (3). Such a definition inevitably poses the question of how long are you willing to wait for equilibrium in cases involving metastability. The answer is that this is determined by the experiment you propose to perform and so, perhaps unfortunately, we are obliged to conclude that a system is pure, for a particular purpose, if further fractionation would not yield products whose use would change the result of the particular experiment.

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Solubility Analysis and the Problem of Purity

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The problem of establishing purity is presented from the point of view of new substances—i.e., uncharacterized beyond proved reproducibility in terms of experimental operations. A definition of purity is developed which leads to the identification of a pure substance with a collection of chemical species, all of which may be thought of as derivable from a single chemical species by means of one or more chemical equations. The method of solubility analysis is presented as a comprehensive technique for the establishment of purity of substances in the above sense.

THE essentials of the problem of establishing the purity of a sample of a substance may be revealed most clearly perhaps in terms of a concrete example. Consider a substance isolated from a biological growth-medium and detected in terms of a single highly specific property, say, its inhibitory effect on the growth of an organism. The impurity of early samples of the substance is easily revealed by the ease with which fractionation is effected, the purification being indicated by the enhancement of the single characteristic property. The process of fractionation, however, results ultimately in decreasing returns. Let it be assumed in the limit that known procedures which result in resolution into fractions showing any observable difference in properties have been exhausted. The specific problem of the purity of the sample may then be formulated in terms of the determination of the extent and the sense in which the sample conforms to criteria to which all known unresolvable substances conform. The general theoretical aspect of the problem is the proof of the necessity and the sufficiency of such criteria for unresolvability.

The practical aspect of the problem is the providing of experimental methods to correspond.

CONCEPT OF PURITY

Preliminary to a consideration of the problem itself is that of defining a pure substance. A definition is to be sought which is comprehensive, suitably flexible in terms of restricted ranges of experimental conditions, and suggestive of experimental methods. It is to correspond so far as possible with intuitive ideas and with a fundamental utility of concept. In the development of a definition with such criteria in mind, attention is to be focused primarily in the direction of chemical requirements, the assumption being made that a consideration of chemical requirements necessarily precedes that of other relevant requirements.

An impure substance is conceived intuitively as a collection of entities which are in some sense independent, a pure substance as one of such entities. The definition is thus resolved into an understanding of an entity and in particular into an under-

standing of the independence of entities. The nature of the concept of purity depends upon the choice which is made for the entities.

To identify an entity with a chemical element would provide a logical and comprehensive scheme, but it forces the conclusion that every chemical compound between distinct chemical elements be regarded as impure. The concept of purity thus reached would lose utility at the start. To identify each entity with a chemical species as represented by a chemical formula— i.e., a formula which represents the properties of the postulated species—forces the conclusion that the substance, liquid water, for example, is impure since it is necessary to postulate the existence of more than one chemical species in order to account with completeness for the chemical properties of water. Such considerations lead one to essay the identification of an entity with a collection of chemical species, all of which may be thought of as derived from a single chemical species as indicated by one or more chemical equations. In addition, the proposed identification of an entity with a collection of chemical species implies that the species are present in definite proportions corresponding to chemical equilibrium, that the time required for attainment of equilibrium is short in comparison with relevant periods of observation, and that thermodynamic criteria for equilibrium between all of the species are met at all times. A collection of chemical species, derivable from a single species, is thus to be identified with an entity—i.e., with a pure substance—provided the collection meets stoichiometric and thermodynamic criteria.

The criterion for the independence of the entities, or alternatively of the independence of the pure substances comprising a system, is obtained from any of the thermodynamic criteria for equilibrium (at constant temperature and pressure) among the various chemical species present. One such criterion is furnished by the set of algebraic equations expressing the fact that the partial molal free energy of a chemical species in a given phase is equal to that of the same species in any other phase which is present at equilibrium, and in addition that the partial molal free energy of a species is equal to the stoichiometric sum of the partial molal free energies of its component species.

This criterion leads to the phase rule: $P + F = C + 2$. Here P is equal to the number of phases as observed, F to the number of degrees of freedom as observed, and C to the number of independent entities as deduced from the relationship—i.e., the number of components in the sense of the phase rule. Thus, if the properties of a single phase are to depend upon two and only two variables, say, the temperature and the pressure, C is necessarily equal to 1. (Specific effects of extent of surface, external fields, orientation, etc., are for the purpose of discussion regarded as irrelevant.) Implicit in this deduction is the condition that all the chemical species represented by the system for which $C = 1$ be present in fixed ratios and satisfy the criteria of thermodynamic equilibrium. The condition $C = 1$ for a system is thus a sufficient condition that the substance comprising the system be pure in the sense under consideration. In making this assertion, the irrelevance of compositional variables—i.e., of variables other than the temperature and the pressure (or of their equivalent)—is assumed to be the crux of every intuitive concept of purity.

The condition that $C = 1$ for a system is not, however, in all cases a necessary condition that the substance of the system be pure. The distinction arises from the fact that in a determination of the number of components it is essential to consider all possible phases of the system which may arise—at least for a restricted range of conditions—provision being made for their appearance in a relevant period of observation, whereas in the establishment of purity it is not necessary to widen consideration to this extent.

For the sake of exposition, consider the case of an intermolecular compound—e.g., a chemical species representable as $X \cdot Y$, say, a double salt. If a second pure substance is added—

e.g., a solvent—the appearance of a phase such as X forces the conclusion that the new system is one for which C is 3 at least. From this it is deduced that C is at least 2 for the system $X \cdot Y$, since it can be reformed from particular entities which are necessarily independent in the larger system and hence independent in the smaller. If any single phase (containing both X and Y) which is obtainable from X and Y corresponds experimentally to an invariant composition, then the two (or higher) component phase so obtained is without loss of generality to be regarded as a pure substance. The justification for the assertion is the obvious irrelevance of compositional variables for a phase found to be invariant as to composition. There may, of course, be more than one such invariant phase containing both X and Y—e.g., $X \cdot Y$, $X \cdot Y_2$, etc. If, on the other hand, single phases (containing both X and Y) which are obtainable from X and Y represent a range of compositions, there is no alternative to the conclusion that such phases are impure. In either case the invariance or noninvariance of the phases containing both X and Y is deducible from experimental relationships found to exist.

The problem of purity as treated above in terms of the phase rule appears straightforward, indeed simple, except perhaps for experimental technique, (1) provided the impurity or foreign entity—i.e., second component—is present as a distinct phase, (2) provided the ratio of the quantities of the two components does not coincide with a certain unique ratio, and (3) provided finally the contaminants are present in substantial quantity, say, greater than 0.1%. The implication is not intended, however, that the specified conditions of the provisos correspond necessarily to insuperable situations, but rather that special consideration may be required for a correct interpretation. For example, the case in which the contaminant is present as a component of a solid solution comes readily within the field of comparatively routine interpretation except for an extreme case of similarity between components as in the case of isotopic contaminants. Likewise in the case of a certain unique ratio of components, the difficulty can usually be turned by a choice of a different temperature or a different solvent, barring the case of a 1 to 1 ratio of optical enantiomorphs. In generalizing from this line of thought, it would appear, however, to be impossible to affirm, without stating a restriction as to the degree of similarity represented by supposed contaminants, as to the singleness of a chemical entity even within the arbitrariness of the working definition and within assigned limits of experimental precision.

If the substance is new, a priori no appeal can be made to chemical analysis beyond the necessary requirement of constancy. Even in the case of substances of known chemical composition, the utility of chemical analysis in samples contaminated possibly with isomers is obviously nil except as a necessary criterion. The degree to which special types of analysis are of use in the case of characterized substances varies widely, depending upon the type of substance. In the case of uncharacterized substances, special methods of analysis prove in general the presence or absence of particular substances.

PHASE-RULE RELATIONSHIPS

The ideas developed above lead to the conclusion that the establishment of the purity of a substance resolves essentially into measurements involving phase-rule relationships and in particular into the study of a system (possibly with an added substance) involving in some essential way the interaction in one or more phases of all the independent entities. Two practical approaches, which on a formal basis appear to be strictly comparable, are (1) via fusion equilibria—i.e., melting points—and (2) via solubility equilibria. Of these two approaches the latter would appear to be more generally applicable in consideration of the lack of stability of many substances at temperatures required for melting, and of the fact that the required experimental technique for solubility analysis is more simple.

A third phase-rule approach to the problem of purity is via multiple extraction (2, 5) between a pair of immiscible solvents— a technique which is powerful, general, and of the greatest utility

in the separation of substances, even substances closely similar in solubility properties. Its failure to reveal, however, the two components present, as an extreme example, in a mixture of optical enantiomorphs of any compositional ratio, reveals clearly the fact that it is not equivalent, in providing a sufficient criterion of purity, to the other two phase-rule approaches, these failing only in case of 1 to 1 compositional ratios in the extreme example of optical enantiomorphs. [The interpretation (as to purity) of multiple extraction results becomes especially difficult in special cases such as (1) that of a substance involving equilibrium between a number of polymeric forms or (2) that of a substance XI_3 giving rise to XI and I_2, these latter having different partition coefficients.]
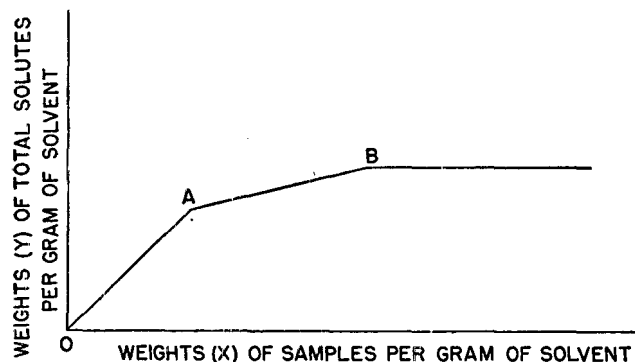

Figure 1. Solubility of Two-Component Substance

No phase-rule approach as such is, of course, practicable for the detection of "traces" of impurities nor of impurities arising from isotopic species of elements. In what follows attention is directed exclusively to the approach to the establishment of purity via a study of solubility equilibria (1, 3, 4). This approach is limited in application to substances for which solubility equilibria conforming to thermodynamic criteria obtain and in particular to substances not subject to irreversible decomposition under the conditions of the required experiments.

PRACTICAL ASPECTS OF SOLUBILITY ANALYSIS

The practical problem of establishing purity by solubility analysis resolves into a determination of the number of components C presented by the sample. Solubility analysis implies the addition of a solvent, this addition giving rise to a system, the number of components of which is $C + 1$. The conclusion from solubility analysis that $C = 1$ is sufficient for the establishment of purity, although it is not in every case a necessary condition.

The phase rule teaches that a one-component substance when added in varying quantity to a fixed quantity of a liquid solvent gives rise, at equilibrium under a fixed temperature and pressure, in turn to a continuous sequence of unsaturated solutions, followed (for a substance of limited solubility) by a single saturated solution, the increasing quantities of the added substance thereafter remaining as excess in the form of a characteristic phase.

Solubility analysis of a substance means the experimental determination under equilibrium conditions of the gross concentration of solutes per unit of solvent for successive additions of varying quantities of the substance to a fixed quantity of solvent. From such data a solubility diagram is constructed by plotting the gross concentration, y, of solutes per unit of solvent against the varying quantities, x, of sample per unit of solvent. This diagram for a substance of one component is then a 45° line from the origin followed by a horizontal line. Alternatively, for a substance composed of two components representing distinct phases,

the phase rule teaches that there is a segment, AB, of the diagram (of slope intermediate between 0 and 1) which lies between the 45° line representing unsaturated solutions and the horizontal line ultimately reached when sufficient of the substance is added to permit the presence of two solid phases (see Figure 1). From the point of view of experimental determination it is highly advantageous to choose a solvent in which the substance is sparingly soluble (say, of the order of 1%). It is then found generally that the intermediate segment of the solubility diagram approximates a straight line.

Due consideration having been given to ensuring that solubility equilibrium has been attained in the sequence of determinations and to the precision of the measurements (for which generally speaking the requirement is high), the question is to be raised as to the conditions under which an intermediate segment would not be observed experimentally even though the substance is significantly impure, C being equal to or greater than 2. Three different types of special conditions are to be mentioned, in each of which in the limit the intermediate segment of the solubility diagram would remain unobservable although a second component is present in significant amount.

First, there is the possibility that the two components, A and B, of a substance (say, each component representing a distinct phase) are present in a ratio which is equal to the ratio of their solubilities at the temperature of the experiment in the solvent chosen (or rather, for the sake of greater generality, in a ratio equal to that obtaining in their invariant solution). Obviously the two components reach saturation at the same point on the diagram, the intermediate segment having contracted to a point. This difficulty can in principle be turned by a different choice of solvent or of temperature, but if the limiting condition is almost met, the intermediate segment is correspondingly short and hence the greater the likelihood of its remaining unobserved although possibly representing a gross proportion of impurity. (The limiting condition is of course met inevitably in the case of 1 to 1 mixtures of optical enantiomorphs.) In consideration of the possibility of the limiting condition's being "almost met," it is in all cases of the greatest importance to determine with the greatest possible precision the intersection of the 45° line with the horizontal line.

The second type of condition preventing the detection by solubility analysis of a second component may be illustrated by the extreme case in which the two components, A and B, differ only in some isotopic constituent of the molecules. The difficulty is to be attributed not only to the near-equality of the properties of the distinct molecular species but also to the fact that the distinct substances form continuous solid solutions. The likelihood of other causes giving rise to similarities between distinct substances approaching in degree that represented by the case of isotopic substances is unknown to the author.

The third type of limiting condition possibly preventing the detection of a second component may be illustrated by a dissociating substance, AB, the contaminating second component being one of the dissociation products, say A. The limiting case would be reached for a ratio A/AB unique in terms of their solubilities. As an illustration of the nature of this difficulty, racemic leucine contaminated with l-leucine to the extent of 10% gives rise to an intermediate segment of initial slope of approximately 1%. More closely coincident conditions may easily give rise to a segment indistinguishable experimentally from one of zero slope.

In the preceding, we have examined a sufficient condition for purity—viz., $C = 1$; we have seen that a solubility diagram consisting of a 45° line followed by a line of zero slope is required in the case C equals 1; and, in particular, we have discussed three limiting cases in which a diagram of this type would be observed even though the number of components is greater than one and the substance therefore impure. We consider next the case in which C is greater than 1, nevertheless it being logical to regard the substance as pure. Solubility analysis itself fur-

nishes the information required in order to conclude that the sample representing a phase containing components X, Y, etc., is invariant as to composition and hence justifiably pure. In particular we are here concerned with the invariance or the non-invariance (as to composition) of a phase containing more than one component, the former condition being indicative of a pure substance, the latter of a solution regardless of the state of aggregation.

The case under consideration may be illustrated by a substance $X \cdot Y$ (say, corresponding to a single phase) which on being added in successively larger quantity to a fixed quantity of solvent gives rise (when first in excess—i.e., at point Q in Figure 2) to a new phase which is distinct from the original phase and which in a simplest case may correspond to one of the dissociation products of $X \cdot Y$ (see Figure 2). The case is that which in phase-rule terminology is referred to as a substance "decomposed by the solvent" or as showing an incongruent solubility. On successive further addition of the substance (Figure 2, $Q \rightarrow Q'$), the gross composition of the solution alters corresponding to a sloping segment. Ultimately there appears an additional phase—viz., that of the original substance—and from this point on ($Q' \rightarrow Q_0$) the solubility diagram is a line of zero slope.

The question under consideration is the purity of the original substance containing X and Y. Any phase containing both X and Y which may be isolated from the system and which is invariant in its composition is by the fact of its invariance one for which compositional variables are irrelevant and which may therefore logically be regarded as pure. There may be more than one such phase—e.g., XY, XY_2, etc. For the sake of exposition we limit consideration to one such phase. The solid phase (say Y) isolated in the range of the intermediate sloping segment is a new phase, and this fact would be ascertained, for example, by subjecting it to a solubility analysis. If the original substance containing X and Y is a phase invariant as to composition, this fact may be ascertained by subjecting the residue (R_0 in Figure 2) from the invariant solution (R in Figure 2) of the original solubility analysis to a further solubility analysis. The solubility diagram so obtained is necessarily different from the original one. Purity of the original sample—i.e., invariance as to composition—is indicated if the solid isolated (in the last solubility analysis) in the range of the intermediate sloping segment is identical as to composition with the original sample—i.e., Q_0 coincident with $X \cdot Y$ in Figure 2.
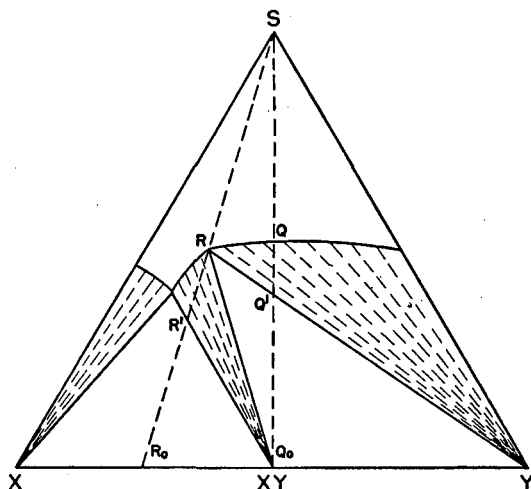

Figure 2.   Solubility Diagram

Thus far we have considered explicitly the problem of purity of substances which exist in phases invariant as to composition, the cases considered dividing, however, into two classes: those in which under a suitably limited range of experimentation the invariant phase presented by the substance was representable as a single component and those in which this was not the case. We turn now briefly to the case in which the phase presented by

the substance is not invariant as to composition, hence necessarily one for which C is greater than 1 and hence also impure. Under solubility analysis such a phase (say of two components) gives rise in turn to a continuous series of unsaturated solutions, followed by a second series of solutions of continuously varying composition in the presence of an excess of the phase representing the substance.

The successive additions of the substance to solvent in this range of the diagram correspond to a partitioning of components between the two continuously varying phases—i.e., between two solutions—one of which may be presumed in the solid state of aggregation. In general, then, the excesses of the added substance isolated at different points represented in the region of the sloping segment of the solubility diagram are of different composition and this fact is ascertained either by subsequent solubility analyses of the phases isolated or otherwise by chemical analysis. In case the components of the substance are of limited solubility in the solid state and if the substance presents besides the phase representing the solid solution a second phase corresponding either to a single component or to a second solid solution, a segment of the diagram of zero slope is observed following the segment representing the partitioning between the solid and liquid solutions.

Thus, in the case of substances contaminated in the form of solid solutions, solubility analysis provides a basis for study, indeed, a basis generally applicable. In this case, however, there are numerous possibilities for coincident compositions, successive additions of the solid solution to a solvent giving rise to no detectable alteration of either phase as to composition. The extreme case is illustrated by a solid solution, the two components of which are isotopically similar. In this case every composition from a practical viewpoint is a coincident composition.

CONCLUSION

The most simple case is that of a mixture of substances, each of one component and each representing a single solid phase, thus excluding solid solutions and intermolecular compounds. In addition, unique compositional ratios are excluded in referring to the most simple case. In the author's experience with a large number of new organic compounds of low molecular weight, the most simple case as defined is that of preponderating frequency. Under solubility analysis, the impurities of a substance falling into the category of the most simple case are revealed in a solubility diagram by a series of sloping segments, followed finally by a segment of zero slope. The number of sloping segments is equal to the number of independent substances presented by the sample. In the case of a solvent in which the solubilities are low, the sloping segments approximate straight lines. In the absence of pronounced mutual influence on the solubilities of the substances, an easy calculation permits an evaluation of the proportion of the impurity. In the most simple case a knowledge of only the existence of a ternary or higher-component phase diagram suffices.

[In the case, however, of a substance composed of $X \cdot Y$ contaminated possibly with $X' \cdot Y$, the problem of purity being the proving of the presence or absence of X' (X and X' closely similar), the system is possibly quaternary and assumptions are required as to the nature of the ternary diagrams (say X-Y-solvent, X'-Y-solvent). Since the sample at hand is $X \cdot Y$ or $X \cdot Y$ + $X' \cdot Y$, the procedure is necessarily stepwise and tentative.]

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Purity and Identity of Polymers

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Because high polymers are difficult to purify and identify, the expressions "purity" and "identity" should be used with great care. The most important impurities and inhomogeneities are: Traces of impurities of low molecular weight such as remnants of solvents, precipitants, catalysts, activators, modifiers, emulsifiers, stabilizers, etc. Groups of atoms which are not characteristic of the polymer itself, such as CH_3, CO, C=C, C—O—C, COOH, etc., but are present in the material in small quantities and influence its behavior noticeably. The existence of a molecular weight distribution curve, which indicates the presence of species having widely different molecular weight. The arrangement of the monomers in vinyl polymers can be head to tail, head to head, or a mixture of both; dienes can polymerize in the 1,4 and 1,2 additions. In some cases a given polymer, such as polyethylene, polyvinyl chloride, polystyrene, etc., can exist in an unbranched and in a branched modification. Recent observations indicate the existence of stereoisomerism and of rotational isomerism in macromolecules.

HIGH polymeric substances are of a rather complicated nature and one should be very hesitant to apply to them definitions and expressions taken from the domain of low molecular weight compounds, which respond much better to our various experimental methods and, hence, are much better known to us. This short article intends to convey an idea of the difficulties in attempting to analyze and characterize natural or synthetic polymers. As a consequence of these difficulties it will appear desirable not to use too freely words such as "pure," "identical," "equal," etc., but, in the characterization and description of a sample, rather to refer briefly to the way in which it was prepared (from a natural source or from a monomeric material) and conditioned. In many cases it is possible to reproduce samples to a remarkable degree by strict observance of their preparation, so that a basis for scientific investigation can be established by sufficiently careful procedures.

LOW MOLECULAR WEIGHT IMPURITIES

Most polymers contain impurities of low molecular weight which are a consequence of the processes of separation in the case of cellulose, starch, or rubber and of preparation in the case of synthetic polymers, and which, in many cases, adhere very tenaciously to the polymeric materials.

Cellulose. Probably the purest form of cellulose is obtained from cottonseed hairs, but even these specimens contain a number of noncellulosic constituents. There are, first, waxy materials distributed on the external and internal surface of the filaments in small proportions (order of magnitude of 1%). They can be removed by extraction with organic solvents down to a negligible amount, but it takes a long time to remove the solvents equally thoroughly because cellulose fibers have a surprising capacity for occluding and tenaciously retaining even hydrocarbons such as benzene or toluene. If drastic drying operations are applied, one may change irreversibly the chemical structure or physical texture of the cellulose sample.

All natural cellulose fibers or membranes contain small amounts (order of magnitude of fractions of 1%) of inorganic salts (sulfates, chlorides, and phosphates), depending upon the soil on which the plant grew (exact spectroscopic analysis of these salts can identify where a given cellulose fiber was grown); their amount can usually be greatly reduced by washing with dilute acids, but again, such acid washes may degrade the cellulose irreversibly and the complete removal of the washing liquid may cause other permanent changes in the chemical structure and physical texture of the original material.

Perhaps the most important and most tenaciously retained impurity in cellulose is water, which under standard conditions is present in proportions of about 10% and can never be completely removed without endangering the integrity of the original material. The term "bone-dry cellulose" refers to a certain drying procedure rather than to the fact that the sample has been freed from all water molecules which are linked to it by secondary valencies. If we submit cellulose to a severe drying operation, we have at present no experimental means for finding out when the last water molecule is removed which is held to the fiber by "physical" forces such as strong polar bonds or hydrogen bridges and when we have started to split off the first "chemically" bound water molecule by forming an ether bond between two adjacent hydroxyl groups in the lattice.

Similar is the situation if we consider starch, which also contains waxy substances, salts, and water or native rubber, which is contaminated by proteins, ester gums, and salts.

In all these cases of purified natural polymers it is common usage to speak of "standard" samples rather than of "pure" materials and to refer to the various steps which have been used to bring the material into its standard form.

Synthetic Polymers. Conditions are not less complicated if we deal with synthetic polymers.

Let us first consider a piece of polystyrene, which was polymerized in block and which represents a water-clear and colorless plastic of very attractive appearance. Nevertheless it contains a number of impurities of low molecular weight.

There are first nonpolymerizable impurities of the monomer such as ethylbenzene, phenylacetaldehyde, and phenyl ethyl alcohol, which are dissolved in the resin, and there is always a certain amount of monomer left which did not enter the polymerization reaction. These impurities may run up to several per cent; their presence does not manifest itself immediately, but they may cause crazing, opacity, and discoloration as time goes on. These volatile impurities can, in most cases, be removed by grinding the block polymer to a fine powder and subjecting it to an extraction process with a liquid in which the polymer is insoluble, whereas the impurities are dissolved. After completion of this operation, removal of the extracting solvent sometimes requires a rather lengthy drying operation which cannot be accelerated substantially without changing the polymer sample irreversibly. The conditions are here similar to those in the drying of cellulose.

If an initiator such as a peroxide has been used in the preparation of the polystyrene block, its remnants are contained in the plastic. They are usually dissolved and do not immediately affect the material, but may have a bad influence on its aging characteristics. As time goes on, and particularly under the influence of heat and light, these peroxidic compounds dissociate

to form radicals, which cause slow reactions to take place in the resin (*41*). Depending upon the conditions, these aging processes can lead to embrittlement or softening of the material and nearly always cause opacity and discoloration. These excess amounts of the polymerization initiator can be removed to a certain extent by solvent extraction, but one can never get rid of them completely in this manner.

Conditions are much worse if a synthetic polymer has been prepared by emulsion polymerization, such as the various types of synthetic rubbers, polyvinyl chloride, or polyvinyl acetate. In these cases the recipe of the polymerization includes initiators, activators, promoters, modifiers, stabilizers, plasticizers, and emulsifiers, which are all contained in the final polymer and represent a whole series of impurities of low molecular weight, some of which are very difficult to remove. Prolonged washing of the rubbery or plastic materials on heated rolls reduces the percentage of some of these impurities substantially but carries with it the danger of an irreversible change of the original polymer under the influence of heat, air, and the catalytically active materials on the rolls.

Experience has shown that a relatively good purification of synthetic polymers can be effected in the following manner.

Make a dilute (1 to 2%) solution of the polymer in a not too high boiling solvent, pass it several times through a glass filter, and then precipitate the polymer at elevated temperature with an appropriate precipitant. In the case of polystyrene, use, for instance, benzene or toluene as solvent and isopropanol as precipitant. Then separate the precipitate from the supernatant liquid by decantation, filtration, or centrifugation and wash the precipitate repeatedly with the hot precipitant. After the washing dissolve the polymer in another solvent (methyl ethyl ketone in the case of polystyrene) and precipitate with a low-boiling precipitant (methanol in the case of polystyrene). Again wash the precipitate and repeat the whole procedure. Finally dry the washed precipitate, which contains now almost no other low molecular weight impurity except the low-boiling precipitant, slowly in vacuo at room temperature to constant weight.

When fractions of several polymers (cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, etc.) were deliberately contaminated with various low molecular weight impurities, it was found that most of them could be removed by the above procedure until they could not be detected by standard analytical methods. [Repeated solution and precipitation of polymers have been common purification practice (*1, 5, 9, 11, 18, 20, 32, 37*).] The most delicate step in the whole procedure is the final drying, because it may lead to irreversible changes of the polymer (cross-linking, degradation) even if it is carried out at room temperature. It appears essential to use in the last precipitation a very volatile precipitant which can be easily removed in vacuo at low temperatures.

The impurities discussed above are not chemically connected with the individual large molecules of the polymer but are only admixed with them, although they are sometimes held back rather tenaciously by strong polar forces or even hydrogen bonds. The complicated nature of polymeric materials, however, has the consequence that there are other, more strongly adherent, more intimately connected impurities in the form of atomic groups, which should not be present in the sample at all if the polymer molecules had exactly the simple and schematic formula which we ascribe to them.

FOREIGN ATOMIC GROUPS IN MACROMOLECULES

We formulate, for instance, polyethylene as a long chain of methylene groups according to
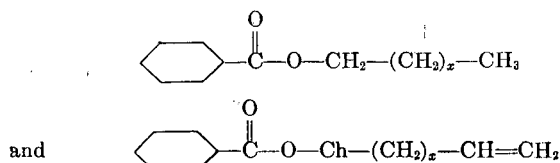
$$\ldots -CH_2-(CH_2)_x-CH_2- \ldots$$

where x is of the order of magnitude of several hundreds or even several thousands, and do not explicitly specify the character of the end groups. It is true that in very long chains (x equal to 10,000 or more) the end groups will play a more and more neg-

ligible role, but in shorter chains (x equal to a few hundred) they may affect important properties, such as dielectric losses, water absorption, etc., rather noticeably. If the polymerization of ethylene is carried out with the aid of a peroxidic catalyst, such as benzoyl peroxide, it is probable that fragments of the catalyst, such as

$$\begin{array}{c} O \\ \| \\ \bigcirc\!\!-C-O- \end{array} \qquad \text{or} \qquad \bigcirc\!\!-$$
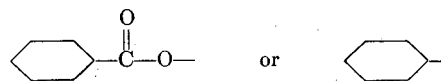
are attached to that end of the macromolecule at which the growth of the chain was started. The character of the other end depends upon the way in which this particular chain was terminated. If the cessation of chain growth occurs by recombination of two growing chains, each of which has a catalyst fragment at its end, the final terminated chain will have such fragments at each of its ends and we have to expect a symmetrical character of the polymer molecule as far as its end groups are concerned. If, however, the two colliding growing chains terminated each other by disproportionation—namely, by the exchange of a hydrogen atom—one chain will have a methyl group at one end, whereas the other chain will have an aliphatic double bond:

$$\begin{array}{c} O \\ \| \\ \bigcirc\!\!-C-O-CH_2-(CH_2)_x-CH_3 \end{array}$$

and

$$\begin{array}{c} O \\ \| \\ \bigcirc\!\!-C-O-Ch-(CH_2)_x-CH=CH_2 \end{array}$$

Finally, if the termination of an individual polymer molecule takes place by chain transfer, the terminated chain end is also occupied by a methyl group and the newly initiated chain starts with an aliphatic double bond. If a chain transfer agent is used, the terminated chain end consists of a methyl group, whereas the new chain is initiated by a fragment of the chain transfer agent (modifier, regulator).

In vinyl polymerization we must therefore, in general, visualize the existence of three or four different types of chain ends, whereas polycondensation products, like polyesters or polyamides and natural polymers such as cellulose, rubber, etc., have, in general, only two different end groups.

Although the number and nature of the chain ends in a given sample depend largely upon the mode of its preparation, we cannot consider these groups to be impurities or accidental occurrences, because they are necessary to make stable molecules out of the growing radical type chains.

However, we have good experimental reason to believe that most polymers contain a certain number of "odd," "foreign," or "accidental" groups in the chain itself. The presence of these groups was established partly by chemical analysis, but mainly by optical methods such as infrared and ultraviolet absorption and by the Raman spectrum (*2, 3, 4, 27, 28, 34, 38, 40, 41, 43*).

It was, for instance, found that polyethylene contains ether bonds, aliphatic double bonds, carbonyl groups, and methyl groups to a much larger extent than explainable by the end groups which contain all these configurations. The percentage of methyl groups in a given sample depends essentially upon the way in which the polymer was prepared; in some cases there is only one methyl group on several hundred methylene groups, in other cases there are as many as one in thirty. The presence of methyl groups in polyethylene is, according to Bryant (*4*) a consequence of branching, which in turn depends upon the mode of polymerization of the monomer. Slightly branched polyethylenes show a high melting point, a high specific gravity, and a distinct tendency to crystallize; they are relatively stiff and brittle and represent excellent barriers against the permeation of water vapor. Highly branched polyethylenes, on the other hand, exhibit lower melting points, are softer, are more reluctant to crystal-

lize, and let water vapor permeate more easily. Thus it is possible to prepare, from one and the same monomer, polymers of widely different properties by introducing different percentages of one of the "odd" groups; it seems that each branch of the chain acts like an ingrown plasticizer molecule.

Similar conditions appear to exist in many other vinyl polymers and copolymers, such as polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polystyrene, etc., where the presence of odd groups has been established experimentally by the methods listed above. These groups not only affect the mechanical, thermal, and electrical properties of the materials in which they are distributed, but appear also to be responsible for their aging characteristics and to act in certain cases as weak spots for the attack of oxygen and moisture in the presence of light and heat (41).

Natural polymers show similar behavior. Cellulose, for instance, is usually considered to consist of linear chains of the following nature:

$$\text{[cellulose chain structure]}$$
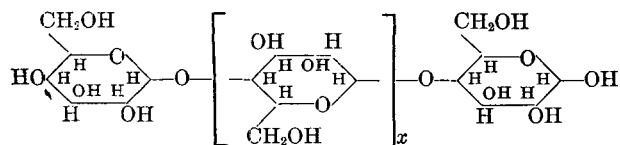
where x has a value of several hundreds or even a few thousands. Careful chemical analysis has shown, however, that all technical samples of cellulose contain nonglucoxidic residues of odd character, such as

$$\text{[chemical structures: COOH, CH}_2\text{OH groups]}$$
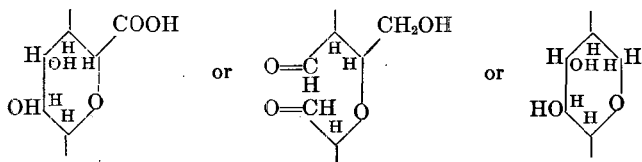
and according to Pacsu also glucose residues in their open chain form, which might provide for the possibility of linking individual chains together by acetalic and hemiacetalic bonds (6, 25, 26, 30, 42, 44).

Most of these groups affect the behavior of the polymer profoundly. Even a few per cent of carboxyl groups increase the swelling of cellulose in water drastically and render the polymer soluble in alkali. Carboxyl groups and aldehyde groups noticeably increase the sensitivity of the adjacent 1,4-glucosidic bond against oxygen in alkaline solution and cause a rapid degradation of the chains which carry these groups at high pH. Their presence is, therefore, in general deterimental to the chemical and mechanical stability of cellulose samples and their analytical determination is of great interest, if one wants to develop methods for the preparation of materials which contain as few as possible of these modified glucose residues.

Natural rubber is usually represented by the formula

$$\text{[natural rubber structure with CH}_3\text{ groups]}$$
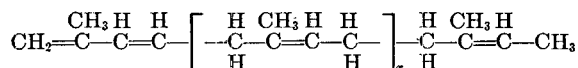
where x is of the order of magnitude of several thousand, but infrared analysis provides evidence that all technical rubbers and all samples which have been purified by various methods contain carbonyl groups and hydroxyl groups, which affect the water absorption of the material and serve as points of attack for various reagents in the process of light and heat aging.

MOLECULAR WEIGHT DISTRIBUTION

Another type of heterogeneity seems to be characteristic of all natural and synthetic high polymers—namely, their polymolecularity.

It was early recognized that practically all macromolecular substances, those which are obtained by purification from natural sources and those which are produced from materials of low molecular weight by polymerization processes, do not consist of a single species of molecules but contain a spectrum of molecules having different molecular weights (22, 37). A few natural polymers, such as certain proteins or resins, may be of comparative homogeneity in the native state, but by the time we have freed them from all their natural relations, they are usually somewhat degraded and represent a more or less wide mixture of species of different molecular weight. The idea of polymolecularity was first derived qualitatively from the general behavior of high polymers, but was later established experimentally and represents an interesting and attractive branch of research in the polymer field (5, 8, 18, 35, 39).

Let us first briefly enumerate the methods with the aid of which the polymolecularity of high polymers can be measured and then discuss a few significant results.

Ultracentrifuge. The oldest and probably still most powerful instrument for investigating the molecular weight distribution is the ultracentrifuge (17, 24, 39). In the hands of Svedberg and his earlier co-workers it proved to be a most valuable tool for studying the uniformity of proteins and protein fractions, but did not permit an equally simple application to linear polymers such as cellulose, its derivatives, and polyvinyl compounds. However, the painstaking work of Svedberg and his more recent associates, Signer (35), Gralén (13), Jullander (16), Rånby and Kinell (29), improved the experimental technique and the theoretical interpretation to such an extent that the ultracentrifuge has been very successfully used to establish the sharpness of cellulose acetate or polystyrene fractions and to demonstrate the molecular heterogeneity of various cellulose samples over a wide range of molecular weight. The method consists in a study of the diffuseness of the meniscus which develops if a very dilute solution of a polymer settles down in a strong ultracentrifugal field. If one makes certain reasonable and probable assumptions regarding the general nature of the molecular weight distribution function, the width of the meniscus in the rapidly rotating cell reflects closely the width of the molecular size distribution of the polymer. This method has a strictly analytical character, inasmuch as there is no opportunity to isolate any of the various molecular species, but gives relatively rapid and reliable information on the polymolecularity of a given system.

Preparatory Fractionation. To get sizable amounts of the individual molecular species, it is necessary to carry out a preparative fractionation of the given material. This is usually done by making a fairly dilute solution (1 to 2%) of the polymer in a solvent of low volatility and by adding a nonsolvent slowly and with moderate stirring. At a certain point of this addition a gelatinous or fluffy precipitate appears, which is separated from the supernatant solution and represents the first fraction. More precipitant is then added to the solution and a second fraction is produced (1, 5, 9, 23, 30). After its separation, still more precipitant is added and a third fraction is obtained. This procedure is continued until the solution contains no more polymer.

Many precautions and conditions have to be observed if the fractionation is to be successful and a large number of comparatively sharp fractions are to be obtained. The liquid from which fractionation is carried out should be neither too good nor too bad a solvent for the polymer; the initial solution should be fairly dilute (2% or less), the added liquid should not be too strong a precipitant, and the whole procedure should be carried out slowly and at constant temperature. Best results are obtained if the fractionation is carried out at approximately constant solute concentration. Badgley has therefore recommended use of a precipitant which is less volatile than the solvent and removal of the solvent from a solvent precipitant mixture at constant temperature by a slow stream of nitrogen. As a con-

sequence, the precipitant concentration increases gradually and the fractions of the solute can be collected in such a manner that the volume of the whole system decreases about in proportion to the amount of solute.

Up to 60 fractions of various polymers have been prepared by this isothermal vacuum fractionation and a relatively good idea of the polymolecularity of the solute (polystyrene, polyvinyl chloride, cellulose acetate) was obtained. The solvent precipitant system must also be carefully chosen from the point of view of the nature of the precipitate. Sometimes the polymer settles down as a highly swollen, gelatinous phase which is very difficult to separate from the supernatant solution and probably contains low molecular weight fractions of the solute occluded. It is essential to operate with a solvent precipitant system which yields the fractions of the polymer in a fluffy or sandy, easily filterable form. In some cases (nitrocellulose, cellulose acetate, polystyrene, polyvinyl chloride, polyisobutylene, rubber, nylon, etc.) such systems have been found and used; in other cases (polyethylene, cellulose xanthate, etc.) no successful fractionation has yet been reported.

A question not yet satisfactorily settled is the polymolecularity of the individual fractions after simple or repeated fractionation. Occasional runs in the ultracentrifuge, turbidity titration, and comparison of number and weight average molecular weight seem to indicate that these fractions are relatively sharp, if a larger number of them (twenty or more) have been isolated from a given polymer under proper precautions. Additional information about the width of so called "sharp" polymer fractions would, however, be very desirable and is necessary in order to be sure of having macromolecules of uniform size. [Recently Merz has used polystyrene containing C^{13} to obtain such additional information (21). These experiments are not yet concluded; they are being continued and the results will be reported at a later date.]

Turbidity Titration. A very interesting and promising analytical method for working out molecular weight distribution curves has been published recently by Morey and Tamblyn (23). These authors follow the precipitation of a polymer from a very dilute solution by measuring the increasing turbidity of the system. If conditions are kept carefully under control, this turbidity is proportional to the amount of the precipitate, and if it is recorded as a function of the amount of precipitant added, one obtains directly an integral weight distribution curve of the dissolved polymer. The turbidity titration has been worked out specifically for cellulose esters and mixed esters such as cellulose acetate, propionate, and butyrate and gives a first insight into the polymolecularity of these materials in a very short time. The actual measurement, not counting the conditioning of the polymer and the preparation and purification of the solution, takes only a few minutes. Morey and Tamblyn checked their method with the aid of a blended sample, which they prepared by mixing known quantities of two relatively sharp fractions, and succeeded in obtaining a molecular weight distribution curve by turbidity titration, which was in remarkable agreement with the actual fractionation of the sample.

Thermal Diffusion. Another very interesting method of establishing the existence of different molecular weight species in a sample and eventually also of effecting a larger scale preparation, was recently suggested by Debye (7). It is based on the principle of thermal diffusion, which has been so successful in separating isotopes of volatile compounds from each other. Debye has shown that in steep temperature gradients the macromolecules of a sufficiently dilute solution should be drawn out into a spectrum of different molecular weight species and it should be possible to separate them from each other solely according to their different masses.

These experimental methods, which make it possible to establish the polymolecularity of a given material, provide a fairly complete picture of the molecular weight distribution function,

but they are all somewhat difficult and time-consuming. The turbidity titration may prove to be an exception, if it is once worked out in all details and with all implications. An abbreviated procedure for getting, at least, a first idea of the polymolecularity of a given material is based on the existence of different averages (or modes) of a molecular weight distribution function. These averages can be determined by different methods and compared with each other. The lowest of them, the number average, can be determined by the chemical analysis of end groups and by any method based on osmotic pressure measurements such as boiling point elevation, freezing point depression, vapor pressure reduction, and direct measurement of the osmotic pressure. The weight average molecular weight is obtained as a result of light-scattering measurements and of the joint evaluation of diffusion and sedimentation rate. [The latter part of this statement is correct only under certain conditions concerning the shape of the dissolved macromolecules and their interaction with the solvent (36).] A third average, the so-called z-average, corresponding to the third mode of the molecular weight distribution function, can be derived from sedimentation equilibrium measurements in the Svedberg ultracentrifuge. If the sample has a narrow molecular weight distribution, the three averages are close together and if the material is very homogeneous, they should be strictly identical. On the other hand, if a polymer has a very wide molecular weight distribution function the ratios M_z/M_w and M_w/M_n assume larger and larger values. In case of the regular distribution function of a polycondensation or polymerization product or of a purified natural material, such as cellulose, the ratio of $M_z:M_w:M_n$ should simply be $3:2:1$ (8, 18). Experimental determination of one of these ratios (usually $M_w:M_n$) gives information as to whether a given material has a narrower or wider molecular weight distribution than normal and provides a certain insight into its polymolecularity.

There exists another molecular weight average which can be obtained from intrinsic viscosity measurements and which is not strictly identical with any of the above-mentioned values. In most cases it is, however, fairly close to the weight average molecular weight.

Application of the methods enumerated above has shown that most natural and synthetic polymers have a rather wide polymolecularity and that the width depends upon the way in which the sample was prepared. It is therefore not permissible to make any statement about the similarity or identity of two samples from the measurement of a single molecular weight average, say from M_n, because it is entirely possible that the weight averages of the two materials may differ appreciably from each other. This shows how cautious one has to be in any statement about polymeric substances that is based on a single measurement, and illustrates the difficulties of a thorough characterization of such materials.

STRUCTURAL DETAILS OF INDIVIDUAL CHAINS

The presence of low molecular weight impurities, the existence of foreign groups in a macromolecular substance, and the polymolecularity of polymers make their identification and characterization rather difficult; however, still other phenomena add to these difficulties—namely, the existence of certain types of isomerisms which occur in macromolecules. These effects have been known for only a relatively short time and the full extent of their occurrence and significance is probably not yet appreciated. As experimental methods for the characterization of polymers gradually improve, the various forms of isomerism will probably be better and better understood.

Arrangement of Units. The first type of isomerism concerns essentially polyvinyl derivatives and has to do with the way in which the monomeric units are arranged in the chain with regard to the sequence of their substituents. It has long been recognized that polyvinyl compounds can occur in two essentially

different types, which Marvel (19) has termed the head-to-tail and the head-to-head forms. In the case of polyvinyl chloride, for instance, these two extreme "isomers" would correspond to the following structures:

head-to-tail

$$X—CH_2—CHCl—[CH_2—CHCl]_x—CH_2—CH_2Cl$$

and head-to-head

$$X—[CH_2—CHCl—CHCl—CH_2]_x—CH_2—CH_2Cl$$
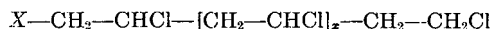
In both formulas X represents some fragment of the initiating catalyst which appears at one end of the macromolecule. It is conceivable that any mixture of head-to-head and head-to-tail arrangement can occur in a given chain and it is in particular possible that the two forms may be randomly distributed in the polymer molecule. Marvel and his co-workers have shown that normal polyvinyl chloride and polyvinylacetate are essentially in the head-to-tail form, whereas certain polyvinyl ketones and polyacrylic derivatives represent head-to-head polymers. The experimental methods, however, are usually such that a small percentage of head-to-head arrangement could not easily be discovered in a principally head-to-tail chain. On the other hand certain physical and chemical properties of a polymer, such as solubility, thermal stability, and resistance to oxygen, might depend upon whether the substituents are regularly alternating in a one-three sequence or whether, at certain points, they are crowded into a one-two arrangement. In fact, Flory has recently demonstrated (10) that in polyvinyl alcohol any one-two glycol configuration can be easily cleaved by the action of periodic acid and represents a potential weak spot in the chain. In order to be fully informed about the properties of a polymer it seems, therefore, that in principle one should know exactly the sequence of the monomer units, down to even a small number of odd arrangements. In some cases there are experimental ways and means of establishing the existence of such flaws, but in most cases new methods will have to be worked out in order to obtain such detailed information about the structure of a polymer chain.

Branching. Another type of structural isomerism is connected with branching. Studies on the kinetics of vinyl polymerization have shown that it is possible for a macromolecule to propagate not only as a strictly linear chain, but as a more or less branched system. Polyethylene seems to be an example of a polymer which can exist in isomeric forms having different degrees of branching, and Bryant has found that this degree depends upon the mode of preparation of the polymer, such as degree of conversion, type of catalyst, etc. It is entirely conceivable that a polymer built of branched chains will differ in many respects from a linear material. Properties such as density, melting point, solubility, crystallizability, and compatibility with plasticizers should be expected to be noticeably different, but it is not easy, in a given case, to correlate the behavior of the material with the degree of branching because we do not have, at present, any general and reliable method of establishing the extent of branching.

Rotational Isomerism. Another type of isomerism of macromolecules appears to be general and may be compared with the rotational isomerism of normal organic compounds. Several years ago it was noticed that correlation of osmotic pressure data and intrinsic viscosities of polystyrene fractions led to different results, depending upon the temperature at which the polymer was prepared (1, 12, 33). The original investigators suggested that a different degree of branching might be made responsible for this effect, but a year later Huggins (15) advanced the idea that all vinyl polymers are subject to stereoisomerism and that this isomerism may be responsible for the different behavior of macromolecules prepared at different conditions.

The experimental evidence at that time was too scanty to arrive at any decisive conclusion, but recently Schildknecht,

Gross, and Zoss (14, 31) discovered a very spectacular case of isomerism of polyvinyl isobutyl ether, which has also been observed with other polyvinyl ethers to a somewhat lesser degree (14, 31). They found that rapid polymerization of these monomers with boron trifluoride at low temperatures leads to rubbery polymers of low softening point, whereas slow polymerization of the same monomer with a moderated catalyst (boron trifluoride and dimethyl ether) yields high softening products of essentially the same molecular weight, which exhibit a distinct tendency for crystallization and are fibrous rather than rubbery. The rubbery and fibrous modifications can be recovered from their respective solutions by a precipitant, at ordinary temperatures. However, if the rubbery polymer is dissolved in a high-boiling solvent, the solution is kept at elevated temperatures for a certain length of time, and the material is precipitated after cooling, the fibrous modification is obtained. The discoverers of this effect explain it by assuming that the comparatively large substituents produce enough hindrance of the rotation about the carbon-carbon bonds of the main chain to stabilize certain strongly kinked configurations of the polymer molecule, which are reluctant to crystallize and are responsible for the rubbery modification.
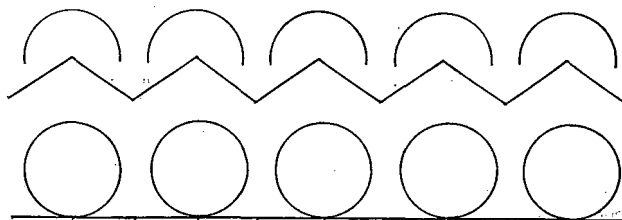

Figure 1

This suggestion opens very interesting new aspects of the behavior of polymers with large substituents.

Let us consider an unbranched simple vinyl polymer such as polyvinyl chloride with head-to-tail sequence. As long as the substituents are small and their mutual interactions weak, there will be moderately hindered rotation about the individual carbon-carbon bonds of the main chain and most geometrical configurations of a macromolecule will have essentially the same potential energy. The actual shape of an individual chain or of each one in a cluster will be mainly determined by entropy considerations and the macromolecules will assume a randomly kinked configuration. The tendency to assume and maintain this most probable shape is responsible for the rubbery character of such polymers.

If the substituents become larger it will no longer be possible to accommodate them in any possible way and if we consider the extended zigzag form of the backbone chain, we will be faced with conditions as represented in Figure 1; its upper part shows a head-to-tail polyvinyl chain viewed perpendicular to the plane in which all carbon-carbon bonds are contained. The points represent schematically the carbon atoms, which are 1.54 Ångström units apart and are of tetrahedral symmetry. Such a planar, zigzag configuration of the backbone chain fits more easily in a simple crystal lattice than any spiralized shape. This is supported by the fact that all normal paraffins and their simple derivatives crystallize in this manner and that polyethylene also favors this type of arrangement. Because of the head-to-tail character of the polymer, all substituents have to be arranged in Figure 1 on the same side of the chain (above or below), if we want to preserve the extended form of the chain and with it the easy crystallizability of the polymer.

There exist, however, two possibilities for the arrangement of the substituents on one side of the backbone chain: one in which all substituents are on the same side of the plane in which the zigzag of the carbon-carbon chain is contained (such as in the lower part of Figure 1) and another in which the substituents are alternately before and behind this plane. If these substituents are large or bulky, the lowest potential energy will be correlated to a chain in which the substituents alternate. The lower parts of Figures 1 and 2 are intended to clarify this situation. In them we look at the chain parallel to the plane which contains the carbon-carbon zigzag. In terms of the upper parts we look at the chain from above and we see now the subsequent car-
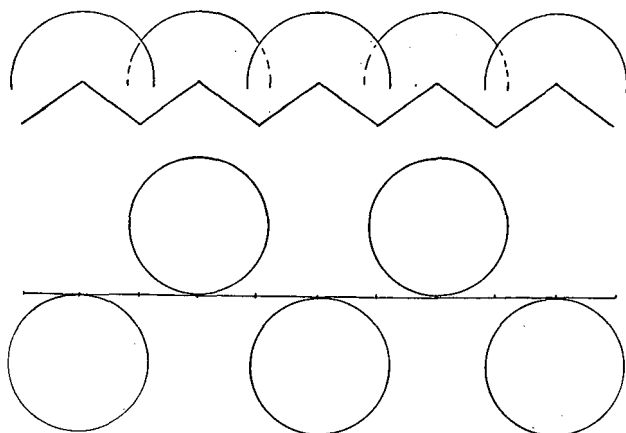
Figure 2

bon atoms of the main chain as a straight line and the substituents emerging from each carbon atom in a zigzag arrangement, right-left-right-left, etc.

The chain configuration as represented in Figures 1 and 2 represents a successful compromise of two facts: a low potential energy because of the zigzag arrangement of the substituents as soon as they are large and bulky (as shown in Figure 2) and easy crystallizability because of the planar zigzag arrangement of the carbon atoms of the main chain.

If a long-chain molecule is formed in the course of a slow and mild reaction, it seems not unreasonable to assume that this is the configuration which will be preponderantly formed. That does not mean that in the reaction mixture all chains will be rigid and straight, but it implies that the macromolecules will have only moderate bends and no sharp or sudden kinks. In the sense of Huggins, this is an arrangement of the substituents in which d and l configurations alternate regularly as one travels along the chain in its straightened out planar zigzag form.

Whenever this chain type is preponderant, we shall expect the high softening, easy crystallizable fibrous modification of a polymer.

Let us now assume that we carry out a rotation of about 150° to 180° about one carbon-carbon bond of the chain, say about bond 6–7 in Figure 2, in such a manner that substituent 4 is now out of phase with the regular right-left alternation as shown in Figure 2. In order to achieve this rotation it will be necessary to move substituent 4 in close proximity to substituents 3 and 5. Because of their bulk or their polar interaction this may require a considerable activation energy, which may assume values of 8000 cal. per mole or more. After rotating the 6–7 bond about 150° or 180°, substituent 4 can again be reasonably accommodated between 3 and 5; not so well as in the straight-chain configuration of Figures 1 and 2, but not very much worse. In terms of potential energy this means that substituent 4 is now vibrating in a potential energy valley, which is not so deep as before (maybe 3000 to 4000 cal. per mole higher) and which is separated from the previous valley by a potential energy barrier of 8000 cal. per mole or more.

The most important change after this rotation is that the main chain now forms a relatively sharp kink at carbon atom 7. Figure 3 gives an idea of this condition. The part of the chain which contains substituents 4 and 5 was swung around and forms an angle of about 90° with its previous direction. This kink is, of course, not strictly permanent, because it can be removed by turning the chain back into its original shape, but it is stabilized by an appreciable activation energy because of the interaction of the substituents and will, therefore, be relatively stable at moderate temperatures.

If a chain once possesses a certain number of such kinks, it will not be straightened out so easily, except by prolonged heating in the dissolved or plasticized state. On the other hand, chains with frequent kinks will fit in a crystal lattice only difficultly and will therefore exhibit a more rubbery character than chains corresponding to Figures 1 and 2.

It seems not too unreasonable to assume that in a rapid reaction the addition of the individual monomers to the growing chain will not always be in accord with the absolute minimum of the potential energy. Once in a while a substituent will not be arranged as Figure 2 prescribes, but as Figure 3 shows for substituent 4. If this happens, on the average, after twenty monomers, the chain is of a very crooked shape, which makes crystallization virtually impossible. If chains of such nature prevail, we have the rubbery modification of a polymer.

Depending upon size and interaction of the substituents, this rubbery modification will exhibit a certain stability but will on prolonged heating eventually isomerize into the fibrous form.

Polyvinyl isobutyl ether seems to be a particularly clear case of this type of isomerism, which has a distinct similarity to the rotational isomerism of ordinary organic compounds, and which according to Schildknecht, Gross, and Zoss seems to exist with other polyvinyl ethers (14). There is evidence that polyvinyl chloride also shows this phenomenon of rotational isomerism to a certain degree. Experiments of Alfrey, Badgley, and Mesrobian have demonstrated that preheating of polyvinyl chloride in solution or in a highly plasticized state increases the tendency of the polymer to crystallize and makes it more difficultly plasticizable. In fact, the kinks of the main chain, which are stabilized by steric hindrance through the substituents, act like an ingrown plasticizer, which is very effective in preventing crystallization and maintaining rubberiness but can be gradually smoothed away by an appropriate heat treatment.
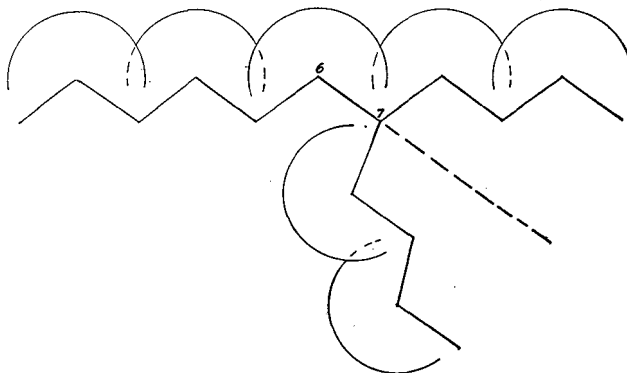

Figure 3

Thus, certain polymers can have different properties if they have been prepared under different conditions, not because of head-to-tail, head-to-head isomerism and not because they represent different degrees of branching, but simply because the substituents are differently arranged in space as we progress along the chain and affect the configuration of the chain as a whole.

CONCLUSION

The preceding paragraphs demonstrate how difficult it is to characterize a polymeric material, even if it consists of only randomly arranged macromolecules which are built up from one single monomer. The difficulties multiply if we consider copolymers of two or more monomers, or if we want to characterize a polymer sample as a whole and not only the polymer molecules as such. In this case we have to take into consideration the mutual relationships of the individual molecules, their geometrical arrangement in space, their axial and lateral orientation, the average size of the ordered domains, etc. We are faced here with similar problems as they occur in metallography and it is obvious that physical methods such as x-ray diffraction, birefringence, and thermal analysis play an important role in the

elucidation of all questions concerning the texture of organic high polymers.

All these facts and considerations are apt to render us rather careful in making any statements about the purity of a polymeric substance or the identity of two or more samples. In most cases it will be advisable to avoid such brief statements and rather to give a short description of what has been done to bring the material into its present condition, what chemical and physical methods have been used to characterize it, and what essential results were obtained by their application.

Certain standards and tests have to be used in industrial practice, such as α-cellulose, heat distortion point, ring and ball test, brittle point, viscosity index, etc., but these expressions have in most cases a purely empirical significance and cannot be considered as strictly reproducible and scientifically well established concepts and procedures. They are very useful and important in the absence of better approaches as long as their empirical character is clearly realized. The present tendency in the field of high polymers is to rationalize these empirical and semiempirical ideas and practices with the aid of well developed methods of physics, physical chemistry, and organic chemistry.

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Pure Compounds from Petroleum

Purification and Purity of Hydrocarbons

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PETROLEUM consists in large part of hydrocarbon molecules of several different types and many different sizes. In the early days, the industry separated petroleum roughly according to molecular size by the process of simple distillation. This operation produced a few broad fractions of petroleum such as gas, gasoline, kerosene, gas oil, and lubricating oil. The properties of each fraction were sufficiently general to satisfy fairly well the requirements of a number of different services.

It was obvious that the value of a given property of one broad fraction was the average of what might be extremely diverse values of that same property for the different types of hydrocarbons present in the mixture. If the types of hydrocarbons having high values of the given property could be separated from those

having low values of the same property, it would be possible to manufacture materials of highly specialized properties rather than average general properties. The special products could then better satisfy the more exacting requirements of modern commerce and industry. In order to attain this objective, however, the petroleum industry would need fundamental information as to the actual composition of its raw material in terms of individual components.

With a few notable exceptions, the researches on the composition of petroleum which had been going on for many years were sporadic and casual. What was needed was a concerted and direct attack on the problem. In 1927, a comprehensive investigation on hydrocarbons in petroleum, sponsored jointly by the

A description of the work at the National Bureau of Standards dealing with the separation of pure compounds from petroleum, and with the purification and determination of purity of hydrocarbons, is presented. This report summarizes this work as carried out in cooperative investigations with the American Petroleum Institute, providing some substance to the philosophy propounded, and reducing to actual practice some of the principles described in the preceding papers of this symposium. The first part of this report surveys the problem of determining the composition of natural petroleum in terms of its individual components, and the latter part describes the work of purifying and determining the purity of hydrocarbons required for use as standard samples for calibrating analytical apparatus and instruments and for measuring needed physical, thermodynamic, and spectrographic properties.

American Petroleum Institute and the National Bureau of Standards, was begun at the National Bureau of Standards under the direction of Edward W. Washburn. This work has been carried on as the American Petroleum Institute Research Project 6. The problem set before the project was essentially one of ascertaining what are the major hydrocarbon constituents in- one representative crude petroleum and then learning how the relative amounts of these major components vary in different petroleums. This work has been in progress continuously since 1927 and has involved a total of about 200 man-years of research (12, 13). (The writer became associated with this work following the death of Edward W. Washburn in 1934.)

SEPARATION OF HYDROCARBONS

The methods used in the work have consisted of the physical processes of fractionation, including distillation in its several variations (regular, at different pressures, and azeotropic), crystallization, extraction, and adsorption, together with accurate measurements of the simple physical properties. The scheme of operation may be described as one of first separating the original petroleum (mixture of paraffin, cycloparaffin, and aromatic hydrocarbons) according to size of molecules and then separating the molecules of the same size according to their type.

In planning a given fractionating operation, attention must be directed to the kind of separation produced by the given fractionating process. For example, separation primarily according to size of molecules is produced by regular distillation, whereas separation primarily according to type of molecules may be produced by extraction, adsorption, azeotropic distillation, or distillation at different pressures. Furthermore, for some processes which fractionate primarily with respect to type of molecules the charging stock must be relatively close-boiling (or substantially homogeneous in size of molecules), while for others the charging stock may be wide-boiling (containing molecules of appreciably different size, as C_5 and C_{10}). An example of the former is azeotropic distillation and of the latter adsorption; extraction is intermediate.

HYDROCARBONS IN ONE PETROLEUM

After exhaustive fractionation with the most efficient and effective methods available, there are obtained various lots or fractions of material, each of which may be substantially one compound or a homogeneous mixture of molecules of the same size and type. As discussed below, a rigorous procedure must be followed in establishing the purity and identity of those materials reported to be single substances. In the case of homogeneous mixtures, the average molecular formula and the type of hydrocarbon may be determined by appropriate observations.

Operating in this way, the following facts have been learned about one representative crude petroleum of intermediate composition (specifically a Ponca, Okla., crude petroleum) (1, 12, 13, 14):

The hydrocarbon molecules are composed of paraffin, cycloparaffin (naphthene), and aromatic groups, or proper combinations of these. (No olefin or acetylene hydrocarbons appear to occur naturally in petroleum in any significant amount.)

In the gas and gasoline fractions (normal boiling range to about 180° C.), the hydrocarbons present in appreciable amount are those of the following classes:

Normal paraffins
Isoparaffins (largely monomethyl isomers with some dimethyl isomers)
Cyclopentane and its alkyl derivatives
Cyclohexane and its alkyl derivatives
Benzene and its alkyl derivatives

Some bicycloparaffins are present in the gasoline fraction in significant but small amount.

In the kerosene fraction (normal boiling range about 180° to 230° C.), the classes of hydrocarbons present include those of the gasoline range together with the following:

Naphthalene and its alkyl derivatives
Tetrahydronaphthalene and its alkyl derivatives
Bicycloparaffins

In the lubricant fraction, although no individual compounds were separated but only mixtures homogeneous with respect to size and type of molecules, it was found that the hydrocarbon molecules are made up of the same component groups that constitute the molecules of the kerosene and gasoline ranges, and that the number of possible combinations of the different groups in one molecule is much greater because of the larger number of carbon atoms per molecule. In the particular representative petroleum studied, the lubricant fraction was characterized by the following points concerning the four broad portions into which, prior to reaching the homogeneous fractions, the lubricant fraction was appropriately separated by type—namely, "wax" (white, solid), "water-white" oil, "extract" oil, and "asphaltic" portion (black, semisolid). (These four broad portions are essentially of different types and are listed in order of decreasing content of hydrogen or increasing content of carbon.)

The wax portion consists essentially of normal paraffins, together with cycloparaffins of 1 or 2 rings with appropriate paraffin side or connecting groups.

The water-white oil portion consists essentially of molecules made up of 1, 2, or 3 cycloparaffin rings with appropriate paraffin side or connecting groups.

The extract oil portion consists essentially of molecules made up of 1, 2, or 3 cycloparaffin rings together with 1, 2, or 3 aromatic rings in the same molecule (when more than 1, usually condensed as in naphthalene and anthracene), with appropriate paraffin side or connecting groups.

The asphaltic portion consists essentially of highly condensed multi-ring aromatics, very low in hydrogen, together with the bulk of the nonhydrocarbon material of the original lubricant fraction.

Contrary to expectations, no purely paraffin hydrocarbons were found in the water-white oil. Normal paraffins occur in the wax portion. Since no isoparaffins were found in the water-white oil, and since the processes of fractionation used could not have segregated the isoparaffins quantitatively in the wax portion, it is believed that no significant amount of isoparaffins was present in this lubricant fraction.

No hydrocarbons composed only of aromatic groups, with appropriate paraffin side or connecting groups, were found in the wax, water-white, or extract portions, and, if present in the lubricant fraction, such purely aromatic hydrocarbons must occur in the black, semisolid, asphaltic portion.

Table I gives a list of the 80 hydrocarbon compounds which have been separated from one petroleum (Ponca, Okla.) by

Table I. List of 80 Hydrocarbons Separated from One Crude Petroleum (Ponca, Okla.)

(American Petroleum Institute Research Project 6 at National Bureau of Standards, as of October 1, 1947)

Formula	Compound	Type[a]	Boiling Point at 1 Atm., °C.	Formula	Compound	Type[a]	Boiling Point at 1 Atm., °C.
CH_4	Methane	Normal paraffin	-161.5	C_8H_{19}	o-Xylene	Benzene	144.4
C_2H_6	Ethane	Normal paraffin	- 88.6	C_9H_{18}	Monocycloparaffin[b]	Cycloparaffin	145.6
C_3H_8	Propane	Normal paraffin	- 42.1	C_9H_{16}	Bicycloparaffin[b]	Bicycloparaffin	146.7
C_4H_{10}	Isobutane	Isoparaffin	- 11.7	C_9H_{20}	n-Nonane	Normal paraffin	150.8
C_4H_{10}	n-Butane	Normal paraffin	- 0.5	C_9H_{12}	Isopropylbenzene	Benzene	152.4
C_5H_{12}	2-Methylbutane	Isoparaffin	27.9	C_9H_{12}	n-Propylbenzene	Benzene	159.2
C_5H_{12}	n-Pentane	Normal paraffin	36.1	C_9H_{12}	1-Methyl-3-ethylbenzene	Benzene	161.3
C_5H_{10}	Cyclopentane	Cyclopentane	49.3	C_9H_{12}	1-Methyl-4-ethylbenzene	Benzene	162.0
C_6H_{14}	2,3-Dimethylbutane	Isoparaffin	58.0	C_9H_{12}	1,3,5-Trimethylbenzene	Benzene	164.7
C_6H_{14}	2-Methylpentane	Isoparaffin	60.3	C_9H_{12}	1-Methyl-2-ethylbenzene	Benzene	165.1
C_6H_{14}	3-Methylpentane	Isoparaffin	63.3	$C_{10}H_{22}$	4-Methylnonane	Isoparaffin	165.7
C_6H_{14}	n-Hexane	Normal paraffin	68.7	$C_{10}H_{22}$	2-Methylnonane	Isoparaffin	166.8
C_6H_{12}	Methylcyclopentane	Cyclopentane	71.8	$C_{10}H_{22}$	3-Methylnonane	Isoparaffin	167.8
C_7H_{16}	2,2-Dimethylpentane	Isoparaffin	79.2	C_9H_{12}	1,2,4-Trimethylbenzene	Benzene	169.3
C_6H_6	Benzene	Benzene	80.1	$C_{10}H_{22}$	n-Decane	Normal paraffin	174.1
C_6H_{12}	Cyclohexane	Cyclohexane	80.7	C_9H_{12}	1,2,3-Trimethylbenzene	Benzene	176.1
C_7H_{14}	1,1-Dimethylcyclopentane	Cyclopentane	87.8	$C_{11}H_{24}$	n-Undecane	Normal paraffin	195.8
C_7H_{16}	2-Methylhexane	Isoparaffin	90.0	$C_{11}H_{16}$	n-Amylbenzene[d]	Benzene	204.1
C_7H_{14}	trans-1,3-Dimethylcyclopentane	Cyclopentane	90.8	$C_{10}H_{14}$	1,2,3,4-Tetramethylbenzene	Benzene	205.0
C_7H_{14}	trans-1,2-Dimethylcyclopentane	Cyclopentane	91.9	$C_{11}H_{16}$	1,4-Dimethyl-2-propylbenzene[d]	Benzene	206.6
C_7H_{16}	3-Methylhexane	Isoparaffin	92.0	$C_{10}H_{12}$	5,6,7,8-Tetrahydronaphthalene	Tetrahydronaphthalene	207.6
C_7H_{16}	n-Heptane	Normal paraffin	98.4				
C_7H_{14}	Methylcyclohexane	Cyclohexane	100.9	$C_{11}H_{16}$	1,5-Dimethyl-2-propylbenzene[d]	Benzene	208.5
C_7H_{14}	Ethylcyclopentane	Cyclopentane	103.5	$C_{11}H_{16}$	1,3,5-Trimethyl-2-ethylbenzene[d]	Benzene	212.3
C_8H_{16}	1,1,3-Trimethylcyclopentane	Cyclopentane	104.9	$C_{12}H_{26}$	n-Dodecane	Normal paraffin	216.3
C_8H_{18}	2,2-Dimethylhexane	Isoparaffin	106.8	$C_{10}H_8$	Naphthalene	Naphthalene	218.0
C_8H_{16}	cis, trans, cis-1,2,3-Trimethylcyclopentane	Cyclopentane	110.4	C_7H_{16}	Phenylcyclopentane[d]	Benzene-cyclopentane	220.7
C_7H_8	Toluene	Benzene	110.6	$C_{11}H_{14}$	2-Methyl-5,6,7,8-tetrahydronaphthalene	Tetrahydronaphthalene	229.0
C_8H_{18}	3,3-Dimethylhexane	Isoparaffin	112.0	$C_{11}H_{14}$	1-Methyl-5,6,7,8-tetrahydronaphthalene	Tetrahydronaphthalene	234.4
C_8H_{16}	1,1,2-Trimethylcyclopentane	Cyclopentane	113.7				
C_8H_{18}	2,3-Dimethylhexane	Isoparaffin	115.6	$C_{11}H_{10}$	2-Methylnaphthalene	Naphthalene	241.1
C_8H_{18}	2-Methyl-3-ethylpentane	Isoparaffin	115.7	$C_{11}H_{10}$	1-Methylnaphthalene	Naphthalene	244.8
C_8H_{18}	2-Methylheptane	Isoparaffin	117.6				
C_8H_{16}	1,1-Dimethylcyclohexane	Cyclohexane	119.5				
C_8H_{16}	cis-1,3-Dimethylcyclohexane	Cyclohexane	120.1				
C_8H_{16}	trans-1,2-Dimethylcyclohexane	Cyclohexane	123.4				
C_8H_{18}	n-Octane	Normal paraffin	125.7				
C_9H_{18}	Tetramethylcyclopentane[b,c]	Cyclopentane	127.4				
C_8H_{16}	n-Propylcyclopentane	Cyclopentane	130.9				
C_8H_{16}	Ethylcyclohexane	Cyclohexane	131.8				
C_9H_{20}	2,6-Dimethylheptane	Isoparaffin	135.2				
C_8H_{10}	Ethylbenzene	Benzene	136.2				
C_9H_{18}	1,1,3-Trimethylcyclohexane	Cyclohexane	136.7				
C_8H_{10}	p-Xylene	Benzene	138.4				
C_8H_{10}	m-Xylene	Benzene	139.1				
C_9H_{20}	2,3-Dimethylheptane[d]	Isoparaffin	140.5				
C_9H_{18}	cis trans,trans-1,2,4-Trimethylcyclohexane	Cyclohexane	141.2				
C_9H_{20}	4-Methyloctane	Isoparaffin	142.5				
C_9H_{20}	2-Methyloctane	Isoparaffin	143.3				
C_9H_{20}	3-Methyloctane	Isoparaffin	144.2				

[a] Compounds classified according to following types: normal paraffin; isoparaffin (branched-chain paraffins); cyclopentane (cyclopentane and its alkyl derivatives); cyclohexane (cyclohexane and its alkyl derivatives); benzene (benzene and its alkyl derivatives); naphthalene (naphthalene and its alkyl derivatives); tetrahydronaphthalene (tetrahydronaphthalene and its alkyl derivatives); benzene-cyclopentane (mixed type); bicycloparaffin. "Cycloparaffin" indicates either "cyclopentane" or "cyclohexane."
[b] Identity not yet determined.
[c] Believed to be 1,1,2,2 or trans-1,1,3,4 isomer.
[d] Identity not yet definitely established.

A.P.I. Research Project 6, as of October 1, 1947. The list includes compounds of the following groups:

Normal paraffins
Isoparaffins, methyl and dimethyl compounds
Cyclopentane and its methyl, dimethyl, trimethyl, tetramethyl, ethyl, and n-propyl derivatives
Cyclohexane and its methyl, dimethyl, trimethyl, and ethyl derivatives
Benzene and its methyl, dimethyl, trimethyl, tetramethyl, ethyl, methylethyl, n-propyl, isopropyl, dimethylpropyl, trimethylpropyl, and n-amyl derivatives
Naphthalene and its methyl derivatives
Tetrahydronaphthalene and its methyl derivatives
Phenylcyclopentane
Bicycloparaffin (as yet unidentified)

A number of additional hydrocarbon compounds are in process of separation from the same petroleum. With regard to the 80 compounds which have so far been separated, the following points should be noted: Some of the best samples have been of high purity (99.8 mole % or better), while for others the purity has been low. Some individual compounds can be separated from petroleum in a state of reasonably good purity with relatively little effort, while for others the separation even of impure lots is a matter of great difficulty. In general, the ones easiest to separate are the ones which can be made purest with least difficulty.

HYDROCARBONS IN DIFFERENT PETROLEUMS

Having learned about the constituents of one representative crude petroleum, it was next desirable to ascertain how the constituents varied from one petroleum to another.

For this investigation, there were selected seven representative crude petroleums from which the gasoline fraction could be appropriately examined with regard to the major individual constituents. These petroleums were selected to represent as wide a variation in composition as possible, at the same time to come from fields of large productivity. The petroleums were all from continental United States and may be characterized as follows: (1) Ponca, Okla., intermediate; (2) East Texas, intermediate; (3) Bradford, Pa., high in paraffins; (4) Greendale-Kawkawlin, Mich., high in normal paraffins; (5) Winkler, Tex., high in isoparaffins; (6) Midway, Calif., high in cycloparaffins (naphthenes); (7) Conroe, Tex., high in aromatics.

By means of appropriate combination of the fractionating process of adsorption with distillation at high efficiency and high reflux ratio, there were determined the amounts of the components in the gasoline fraction of the seven representative crude petroleums, covering the paraffins and cycloparaffins normally boiling up to 102° C. and the alkylbenzenes normally boiling up to about 172° C. On the basis of the data obtained in this work, the following conclusions were made with regard to the hydro-

carbons in different petroleums (referring to all compounds normally boiling to 102° C. and to the alkylbenzenes up to about 172° C., (2, 3):

The gasoline fraction of different crude petroleums is composed of the same hydrocarbons, the differences from one petroleum to another being essentially differences in the relative amounts of the classes of hydrocarbons.

The gasoline fraction of different crude petroleums may be characterized by specifying the relative amounts of the following five classes of hydrocarbons:

Normal paraffins
Isoparaffins
Cyclopentane and its alkyl derivatives
Cyclohexane and its alkyl derivatives
Benzene and its alkyl derivatives

Within each of the above classes, the individual hydrocarbons occur in proportions which are usually of the same magnitude for different petroleums.

On this basis, it is usually possible to predict the magnitude of the amounts of the individual hydrocarbons in the gasoline fraction of petroleum when the relative amounts of the five classes of hydrocarbons are known (paraffins and cycloparaffins to 102° C. and alkylbenzenes to 175° C.), or, alternatively for each class, when the amount of one of the main components of that class is known.

IDENTIFICATION AND PURITY OF SINGLE SUBSTANCES

Before attempting to identify a material separated from petroleum as a given compound by comparison of its properties with those of known pure compounds, it is necessary to prove that the material is substantially a single substance and not a mixture. If a logical sequence of fractionating processes, including distillation at high efficiency, has been followed, the given material will consist of molecules of the same size and type—that is, a mixture of isomers. In some cases, one of the isomers will constitute the bulk of the material, which may then be considered substantially one compound.

In deciding upon the property which is to be used in establishing the fact that the material is or is not substantially one compound, consideration must be given to the following facts:

The material is substantially constant-boiling as a result of its having been produced by a sequence of fractionating processes involving high-efficiency distillation. Therefore, examination of the boiling point as a function of the percentage of the sample vaporized or condensed will be of little or no value in this connection.

The minor components present with the major component will normally be isomers of the latter, as a result of the material's having been well fractionated by type of molecule. The isomers will have values of the density, refractive index, and similar properties, very nearly the same as those of the major component, so that these properties will be of little or no value in this connection. Furthermore, such isomeric minor components will constitute the very compounds which will be most likely to form with the major component a substantially ideal solution.

One of the most effective methods for evaluating the purity of chemical substances is that involving determination of the freezing point, with appropriate observation of the temperature of the liquid-solid equilibrium as a function of the fraction of sample frozen or melted.

In the absence of information as to the identity of the impurities or minor components associated with the parent substance, or of the identity of parent substance as well as the impurities, it appears that the freezing point is the only property which may be utilized to give a quantitative estimate of the purity.

Whenever the identities of the major component and of its impurities are known, the amounts of the major and minor components can be satisfactorily determined by means of spectrometric measurements (infrared, ultraviolet, Raman, or mass, as appropriate), provided there are available for calibration of the given spectrometer pure standard samples of the major component and each of the minor components.

In the problem of identifying and determining the purity of individual hydrocarbons separated from petroleum, the following

cases occur, in order, as knowledge of the material being investigated increases:

At first, no information is available as to the chemical constitution of the material except a knowledge of the elements which compose it. In this case, the investigation may proceed as follows:

The fact that the material separated is substantially a single substance and not a mixture is established. This may be done, as described below, by suitable observations of the temperature of the liquid-solid equilibrium as a function of the fraction of the sample frozen or melted. Such observations also serve to determine, within appropriate limits, the amount of impurity in the given sample.

By measurements of elemental composition and molecular weight, the molecular formula of the substance is determined.

Measurements are made of the simple physical properties of the freezing point (this property will usually already have been measured in the determination of purity), boiling point, density, and refractive index. The foregoing properties are necessary. The following properties may also be determined if equipment is available: viscosity, solubility in a proper solvent, critical solution temperature in a proper solvent.

The simple physical properties of the given substance are compared with the same properties of known pure compounds of the same molecular formula. If adequate matching can be made of the freezing point, refractive index, and density of the given substance with a known pure compound of the same molecular formula, the identification may be considered substantially complete.

If, however, the identification just outlined cannot be made, it will appear that the given substance is not identical with any known compound of the same molecular formula and further steps must be taken to complete the identification, as follows:

Measurement is made of the spectrographic properties, including infrared absorption and ultraviolet absorption. The Raman spectra and mass spectrometer pattern may also be determined.

By analysis and comparison of the physical and spectrographic properties of the unknown substance with those of known compounds of the same molecular formula, it will be possible to establish the identity of the group of isomeric compounds to which the unknown substance belongs. It should be possible also to establish the several most probable compounds with which the unknown may possibly be identified.

Arrangements are made for the synthesis of the most probable compounds in turn, until one is prepared, the properties of which match those of the substance separated from petroleum sufficiently well to establish the identity.

After sufficient information has been obtained as to the types of components which constitute a given fraction or boiling range of petroleum, subsequent examination of such material can be greatly simplified by the elimination of certain steps. In most cases, for example, it becomes unnecessary to make an elemental analysis or determine the molecular weight.

Whenever all the possible components present in significant amount in any given fraction of petroleum are known, and when reliable values are available for the simple physical properties of pure samples of the possible components, the identification of a substance separated from the given fraction becomes a relatively simple matter. In such case, the procedure would be to establish the fact that the material separated is substantially a single substance, measure its simple physical properties, and match these physical properties with those of one of the possible components. In many cases, spectrographic identification can be made more readily than by measurement of the simple physical properties.

CHARACTERIZATION OF HOMOGENEOUS MIXTURES OF HYDROCARBONS

In the higher boiling fractions of petroleum, such as the gas oil and lubricant portions, the isolation of individual compounds (except for the normal paraffins) will be extremely difficult. In such cases, the fractionation will usually be halted at the stage where there are produced homogeneous fractions of molecules of substantially the same size and type. In order to characterize such materials, the following procedure may be followed:

Measurements are made of the properties of boiling point (at an appropriate pressure), density, refractive index, refractive
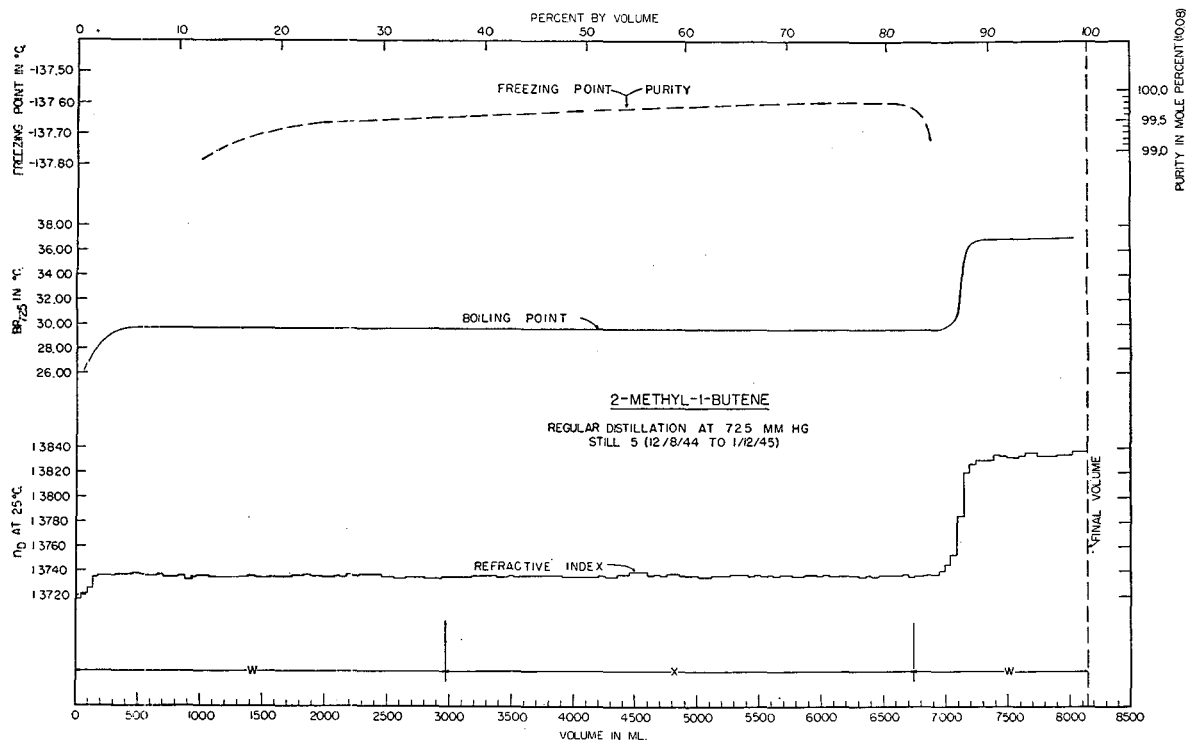
Figure 1. Results of First Distillation of 2-Methyl-1-butene

Regular distillation at 725 mm. of mercury.   Still 5 (12/8/44 to 1/12/45)

dispersion (for appropriate wave lengths), viscosity, critical solution temperature in one or more appropriate solvents, infrared absorption (normally in the range 2 to 15 microns), ultraviolet absorption (normally in the range 0.2·to 0.4 micron or 2000 to 4000 Ångström units), elemental composition, and average molecular weight.

With the above data, it is possible to establish the molecular formula, and, by proper analysis, combination, and correlation of these data with values for known pure compounds, to determine the type of hydrocarbons constituting the homogeneous mixture, as paraffin, cycloparaffin, bicycloparaffin, benzene derivative, naphthalene derivative, tetrahydronaphthalene derivative, etc.

PRINCIPLES INVOLVED IN PURIFICATION OF HYDROCARBONS

We now turn to a discussion of the purification of hydrocarbons for the purpose of producing standard samples for calibrating analytical apparatus and instruments, such as spectrometers, or special samples for the measurement of needed physical, thermodynamic, or spectrographic properties.

In preparing the initial concentrate of a given compound for further purification, careful consideration must be given to the possible components that will be associated with the desired compound in the initial concentrate. In general the source of the initial concentrate, whether produced synthetically in the laboratory, manufactured in plant processing, or separated from a natural source, should be such that the unwanted components (impurities) may all be largely removable with the application of proper fractionating processes of high efficiency. Much time and effort can frequently be saved by judicious choice of the source of the material.

Usually the initial concentrate of the given compound is subjected by the preparing laboratory to a simple purification by distillation. All the material from this processing which corresponds to the "temperature-volume flat" appropriate to the given compound is assumed to consist substantially of the given compound. At this stage, the impurities in the material will be largely isomeric or closely related compounds and may frequently amount to as much as 5 or 10% of the sample.

In this laboratory, the target set for the purity of the final best lot of each hydrocarbon purified is 99.8 mole % or better. In planning the purification process to be followed in attaining the desired objective, the following points must be kept in mind:

Advantage must be taken of all the possible fractionating processes which may be successfully used in the laboratory without undue loss of material and at a cost that is not prohibitive.

The practical purification processes available today for laboratory operation on hydrocarbons include:

Regular distillation
Azeotropic distillation
Distillation at different pressures
Adsorption
Crystallization

The conditions for each fractionating process should be selected to yield maximum separation of the components.

If more than one kind of fractionating process is used in a given purification, it is important that the fractionating processes be used in proper sequence.

In order to determine quantitatively the extent of the separation produced by a given fractionating process, a suitable property must be selected for measurement on the various fractions of the product.

The property selected to indicate the extent of the separation must be one which can be readily measured and which will be sufficiently sensitive to disclose changes of 0.01 or less mole per cent in the content of impurity in the fractions of the product.

Since the impurities are largely isomeric or closely related compounds, the properties of boiling point, refractive index, and density will be of little value in disclosing changes in the amount of impurity, since the values of these properties for both the major component and its impurities will not be greatly different. Furthermore, differences in the values of such properties, even when large enough to be measurable, cannot be translated quantitatively into changes in amount of impurity without knowledge of the identities and relative amounts of the impurities.

The freezing point is the one property which can be used in most cases to disclose changes in the amount of impurity in various lots of the major component without knowing the identities of the impurity and without regard to how nearly the same are the values of the freezing point for the major component and its impurities.

For measurement of freezing points for the purpose of disclosing changes in purity, the freezing points must be determined with a precision approaching 0.001° C. for compounds having normal or large heats of fusion. For compounds having small heats of fusion, the precision need not be so good.

PROCESSES OF PURIFICATION

The processes of purification systematically used in this work in this laboratory are regular distillation, azeotropic distillation, distillation at different pressures, adsorption, and crystallization (8, 9, 19).

Regular distillation is used to produce a constant-boiling product, and, in the absence of azeotropic mixtures, serves to remove from the main component all except the very close-boiling impurities. Usually this is the operation to which the original concentrate is first subjected.

Azeotropic distillation is used primarily for the following purposes:

To remove impurities of a different type from the main component, as paraffins from cycloparaffins, olefins from paraffins, aromatics from paraffins, aromatics from cycloparaffins, etc.

To remove isomeric or closely related impurities from a paraffin, cycloparaffin, olefin, or aromatic hydrocarbon.

To reduce materially the amount of material held up in the column during distillation by selection of a suitable lower-boiling azeotrope-forming substance.

To permit distillation of all the wanted material overhead as distillate by using an excess of the azeotrope-forming substance.

Distillation at different pressures is used to remove from the main component an impurity which has at the standard distilling pressure a boiling point very close to that of the main component but which at a different (usually lower) pressure has a boiling point sufficiently different from that of the main component to permit removal of a substantial amount of the impurity.

Adsorption is used to separate hydrocarbons by means of differences in adsorbability, with fractionation occurring between the liquid phase and the solid adsorbed phase. With silica gel as the adsorbent, it is difficult to prevent polymerization and isomerization of olefin hydrocarbons, and the process of adsorption with silica gel is at present normally limited to paraffin, cycloparaffin, and aromatic hydrocarbons. The process of adsorption is used primarily for the following purposes:

To remove water and nonhydrocarbon impurities from paraffin, cycloparaffin, and aromatic hydrocarbons.

To remove aromatic hydrocarbons from paraffin and cycloparaffin hydrocarbons.

In some cases, to remove isomeric and related impurities from a paraffin, cycloparaffin, or aromatic hydrocarbon.

The process of crystallization is one in which crystals of the main component are produced in the liquid phase of the hydrocarbon alone or in the liquid phase of the hydrocarbon plus a suitable solvent. The liquid phase is removed from the solid phase by centrifuging with the crystals being retained on, and the liquid passing through, a fine screen. Theoretically, the solid phase should contain no impurity, but actually it is usually contaminated with some of the liquid phase, and repeated operation becomes necessary to produce material of the highest purity. Because the process of crystallization is not readily adapted to routine operation as in the case of the processes of distillation and adsorption, crystallization is given less preference and is normally used only when it is not possible to produce material of the desired purity by any combination of the other methods.

PURIFICATION OF A.P.I.-STANDARD AND A.P.I.-N.B.S. HYDROCARBONS

In the purification of A.P.I.-Standard and A.P.I.-N.B.S. hydrocarbons at the National Bureau of Standards, preference is given to the use of regular and azeotropic distillation because of the saving of the time of the professional personnel.

The procedure followed in the process of purification by distillation and determination of purity by measurement of freezing points can be illustrated by considering a given compound.

The starting material for 2-methyl-1-butene was 8.3 liters of hydrocarbon, supplied by the Research Laboratories of the General Motors Corporation and estimated by them to be about 90% pure in 2-methyl-1-butene. The 8.3 liters of starting material were charged into column 5 and the distillation, running 24 hours per day, 7 days per week, at a reflux ratio of 125 to 1 and with a rate of collection of distillate of 12.5 ml. per hour, was concluded 38 days later. The distillation time was 840 hours, with about 30 hours to reach equilibrium at the start. The records from the distillation yielded accurate values of the boiling point, to the nearest 0.01° C. at the given controlled pressure of 724.5 mm. of mercury, of the distillate as a function of its volume. The refractive index, n_D at 25° C., of each of the fractions of distillate was measured to ±0.0001, using N.B.S. Standard samples of 2,2,4-trimethylpentane, methylcyclohexane, and toluene as reference substances, on Valentine refractometers, Abbe-type, graduated directly to 0.0001. The purity of four selected fractions was determined by measurement of freezing points, as described below. From the freezing points of these four fractions, a curve was constructed giving the freezing point of the distillate as a function of its volume over the range of higher purity.

Figure 1 gives for the distillate, as a function of its volume, plots of the refractive index (n_D at 25° C.), the boiling point (in ° C. at 724.5 mm. of mercury), and the freezing point (in ° C. in air at 1 atmosphere). The freezing point–volume plot also represents the purity of the distillate as a function of its volume (see scale at upper right in Figure 1).

From the first distillation, it is seen that 3.45 liters of material of 99.7 mole % purity, X in Figure 1, were available for the second distillation. This material was charged into column 13 and the distillation, at a reflux ratio of 145 to 1 and with a rate of collection of distillate of 8.5 ml. per hour, was concluded 26 days later.
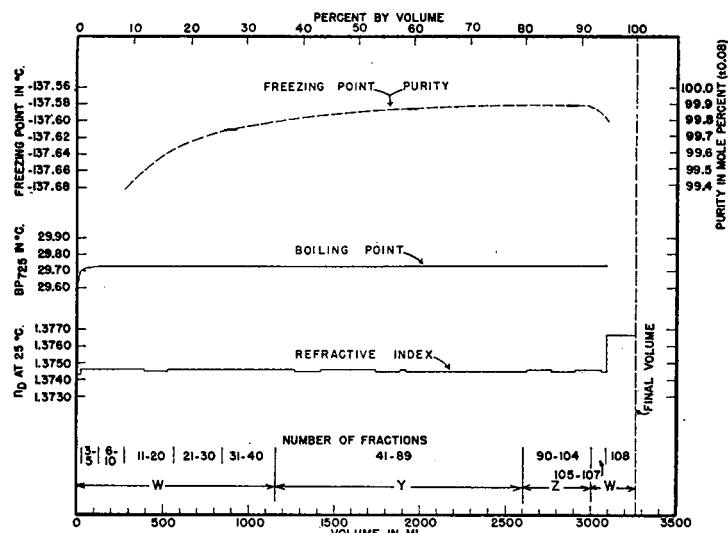

Figure 2.   Results of Second and Final Distillation of 2-Methyl-1-butene

Regular distillation at 725 mm. of mercury.   Still 13 (2/7/45 to 3/5/45)

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The distillation time was 624 hours, with about 30 hours to reach equilibrium at the start. As before, measurements and plots were made of refractive index, boiling point, freezing point, and purity, with the results shown in Figure 2. The part marked Z was taken as the A.P.I.–N.B.S. sample and the parts marked Y were taken as the material for the standard sample. The material marked W in Figures 1 and 2 was returned to the supplier. The final products for this compound consisted of an A.P.I.–N.B.S. sample having a volume of 0.40 liter and a purity of 99.89 ± 0.08 mole % and an A.P.I.–Standard sample having a volume of 1.42 liters and a purity of 99.86 ± 0.08 mole %.

In connection with the purification of hydrocarbons to a high degree of purity, the following points are to be noted: (a) A logical simple purification following the original synthesis or other preparation of a given hydrocarbon concentrate will usually remove all impurities except more or less close-boiling isomers; (b) an impurity of several per cent of close-boiling isomers will have relatively little effect on the boiling point, refractive index, or density,

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a (A) following name of compound indicates that it is first sample of given compound, second sample of which is labeled (B).
b Approximate.
c Abbreviations represent following laboratories: APIRP45. American Petroleum Institute Research Project 45 (formerly American Petroleum Institute Hydrocarbon Research Project) at Ohio State University, Columbus, Ohio.
Penn State. Hydrocarbon Laboratory and American Petroleum Institute Research Project 42, Pennsylvania State College, State College, Pa.
APIRP6. American Petroleum Institute Research Project 6 at National Bureau of Standards, Washington, D. C.
Atlantic. Atlantic Refining Co., Philadelphia, Pa.
Barrett. Barrett Division of Allied Chemical and Dye Corp., New York, N. Y.
Calif. Res. Corp. California Research Corp., Richmond, Calif.
Dow. Dow Chemical Co., Midland, Mich.
Ethyl. Ethyl Corp., Detroit, Mich.
General Motors. General Motors Corp., Detroit, Mich.
Gulf-Mellon. Gulf Oil Co. fellowship at Mellon Institute of Industrial Research, Pittsburgh, Pa.
Houdry. Houdry Process Corp., Marcus Hook, Pa.
Humble. Humble Oil and Refining Co., Houston, Tex.
Kellogg. M. W. Kellogg Co., New York, N. Y.
Monsanto. Monsanto Chemical Co., Dayton, Ohio.
NACA. National Advisory Committee for Aeronautics, Aeronautica Engine Research Laboratory, Cleveland, Ohio.
Phillips. Phillips Petroleum Co., Bartlesville, Okla.
Socony-Vacuum. Socony-Vacuum Laboratories, Paulsboro, N. J.
Std. Oil Dev. Standard Oil Development Co., Elizabeth, N. J.
Std. (Ind.). Standard Oil Co, (Indiana), Whiting, Ind.
Tide Water Assoc. Tide Water Associated Oil Co., Associated, Calif.
d By purchase of commercially available material.

Table II. A.P.I.–N.B.S. Hydrocarbons Completed July 1, 1943, to June

Formula	Compound*a*	Volume*b* Prepared, Ml.	Purity, Mole %	Source of Starting Material*c*
	Paraffins			
C_5H_{12}	*n*-Pentane	370	99.85 ± 0.07	APIRP6*d*
	2-Methylbutane (isopentane)	370	99.85 ± 0.06	APIRP6*d*
	2,2-Dimethylpropane (neopentane)	250	99.982 ± 0.012	Calif. Res. Corp.
C_6H_{14}	*n*-Hexane	375	99.89 ± 0.05	APIRP6
	2-Methylpentane	325	99.97 ± 0.02	APIRP6
	3-Methylpentane	255	(99.90 ± 0.08)*e*	APIRP6
	2,2-Dimethylbutane	290	99.95 ± 0.03	APIRP6*d*
	2,3-Dimethylbutane	275	99.93 ± 0.03	Std. (Ind.); Kellogg
C_7H_{16}	*n*-Heptane	380	99.94 ± 0.05	APIRP6*d*
	2-Methylhexane	300	99.82 ± 0.07	Ethyl
	3-Methylhexane	325	(99.80 ± 0.15)*e*	Ethyl
	3-Ethylpentane	260	99.94 ± 0.03	APIRP45
	2,2-Dimethylpentane	275	99.81 ± 0.06	Socony-Vacuum
	2,3-Dimethylpentane	291	(99.80 ± 0.15)*e*	General Motors
	2,4-Dimethylpentane	250	99.88 ± 0.05	APIRP6
	3,3-Dimethylpentane	465	99.78 ± 0.18	APIRP45
	2,2,3-Trimethylbutane (A)	360	99.95 ± 0.02*f*	General Motors
	2,2,3-Trimethylbutane (B)	260	99.991 ± 0.008	General Motors
C_8H_{18}	*n*-Octane	325	99.95 ± 0.04	APIRP6*d*
	2-Methylheptane	144	99.66 ± 0.18	APIRP45
	3-Methylheptane	185	99.62 ± 0.23	APIRP45
	4-Methylheptane	230	99.89 ± 0.07	APIRP45
	3-Ethylhexane	286	(99.75 ± 0.20)*e*	APIRP45
	2,2-Dimethylhexane	192	99.77 ± 0.11	APIRP45
	2,3-Dimethylhexane	205	(99.75 ± 0.20)*e*	APIRP45
	2,4-Dimethylhexane	365	(99.75 ± 0.20)*e*	Penn State
	2,5-Dimethylhexane	355	99.73 ± 0.09	Penn State
	3,3-Dimethylhexane	250	99.75 ± 0.20	APIRP45
	3,4-Dimethylhexane	151	(99.75 ± 0.20)*e*	APIRP45
	2-Methyl-3-ethylpentane	218	99.78 ± 0.11	APIRP45
	3-Methyl-3-ethylpentane	235	99.93 ± 0.04	APIRP45
	2,2,3-Trimethylpentane	330	99.68 ± 0.20	General Motors
	2,2,4-Trimethylpentane (A)	350	99.88 ± 0.05	APIRP6*d*
	2,2,4-Trimethylpentane (B)	180	99.89 ± 0.05	APIRP6*d*
	2,3,3-Trimethylpentane	250	99.79 ± 0.08	Penn State
	2,3,4-Trimethylpentane	380	99.83 ± 0.06	APIRP45
C_9H_{20}	*n*-Nonane	305	99.94 ± 0.04	APIRP6
	2,2,4-Trimethylhexane	195	99.75 ± 0.20	Penn State
	2,2,5-Trimethylhexane	250	99.86 ± 0.04	APIRP6
	2,3,3-Trimethylhexane	156	99.93 ± 0.06	Penn State
	2,3,5-Trimethylhexane	225	(99.75 ± 0.20)*e*	Penn State
	2,4,4-Trimethylhexane	248	99.73 ± 0.11	Penn State
	3,3-Diethylpentane	152	99.987 ± 0.011	APIRP45
	2,2,3,3-Tetramethylpentane	150	99.940 ± 0.020	APIRP45
	2,2,3,4-Tetramethylpentane	295	99.976 ± 0.014	NACA
	2,2,4,4-Tetramethylpentane	165	99.89 ± 0.08	NACA
	2,3,3,4-Tetramethylpentane	385	99.956 ± 0.037	NACA
$C_{10}H_{22}$	*n*-Decane	415	99.977 ± 0.018	APIRP6*d*
	Aromatics			
C_6H_6	Benzene	450	99.963 ± 0.020	APIRP6*d*
C_7H_8	Methylbenzene (toluene)	330	99.95 ± 0.03	Humble
C_8H_{10}	Ethylbenzene (A)	330	99.83 ± 0.05*g*	Monsanto
	Ethylbenzene (B)	700	99.972 ± 0.020	APIRP6*d*
	1,2-Dimethylbenzene (*o*-xylene) (A)	280	99.963 ± 0.013*h*	Std. Oil Dev.
	1,2-Dimethylbenzene (*o*-xylene) (B)	650	99.992 ± 0.006	Std. Oil Dev.
	1,3-Dimethylbenzene (*m*-xylene) (A)	240	99.85 ± 0.05	APIRP45
	1,3-Dimethylbenzene (*m*-xylene) (B)	160	99.96 ± 0.03	APIRP6*d*
	1,4-Dimethylbenzene (*p*-xylene) (A)	350	99.94 ± 0.03	APIRP45
C_9H_{12}	*n*-Propylbenzene (A)	220	99.71 ± 0.08	Dow
	n-Propylbenzene (B)	340	99.80 ± 0.08	APIRP6*d*
	Isopropylbenzene	350	99.96 ± 0.03	Monsanto
	1-Methyl-2-ethylbenzene	250	99.76 ± 0.07	APIRP45
	1-Methyl-3-ethylbenzene (A)	45	99.77 ± 0.15	APIRP45
	1-Methyl-4-ethylbenzene	275	99.94 ± 0.03	NACA
	1,2,3-Trimethylbenzene (A)	190	99.80 ± 0.04	APIRP6
	1,2,3-Trimethylbenzene (B)	153	99.990 ± 0.009	APIRP45
	1,2,4-Trimethylbenzene (A)	400	99.68 ± 0.20	APIRP6
	1,2,4-Trimethylbenzene (B)	280	99.70 ± 0.20	NACA
	1,3,5-Trimethylbenzene	260	99.96 ± 0.02	APIRP45
$C_{10}H_{14}$	*n*-Butylbenzene (A)	260	99.91 ± 0.08	APIRP45
	n-Butylbenzene (B)	375	99.91 ± 0.08	NACA
	Isobutylbenzene (A)	240	99.86 ± 0.09	APIRP45
	Isobutylbenzene (B)	337	99.88 ± 0.09	NACA
	sec-Butylbenzene (A)	300	99.69 ± 0.06	APIRP45
	sec-Butylbenzene (B)	132	99.93 ± 0.06	NACA
	tert-Butylbenzene (A)	360	99.95 ± 0.03	APIRP45
	tert-Butylbenzene (B)	365	99.943 ± 0.033	NACA
	1,3-Diethylbenzene (A)	150	99.92 ± 0.04	Dow
	1,3-Diethylbenzene (B)	175	99.95 ± 0.04	NACA; APIRP45

e Estimated.
f Revised; originally reported as 99.97 ± 0.02.
g Revised; originally reported as 99.84 ± 0.09.
h Revised; originally reported as 99.990 ± 0.007.
i Revised; originally reported as 99.977 ± 0.010.
j Revised; originally reported as 99.92 ± 0.04.
k Revised; originally reported as 99.95 ± 0.03.

30, 1947, by the American Petroleum Institute Research Project 6

Formula	Compound[a]	Volume[b] Prepared, Ml.	Purity, Mole %		Source of Starting Material[e]
	Alkylcyclobutanes				
C_6H_{12}	Ethylcyclobutane	294	99.92	± 0.06	APIRP45
	Alkylcyclopentanes				
C_5H_{10}	Cyclopentane (A)	415	99.971	± 0.009[i]	APIRP45
	Cyclopentane (B)	300	99.974	± 0.009	Tide Water Assoc.
C_6H_{12}	Methylcyclopentane	380	99.84	± 0.06	Houdry
C_7H_{14}	Ethylcyclopentane (A)	200	99.89	± 0.04[j]	APIRP45
	Ethylcyclopentane (B)	375	99.92	± 0.04[k]	APIRP45; Penn State
	1,1-Dimethylcyclopentane	260	99.97	± 0.02	Penn State
	cis-1,2-Dimethylcyclopentane	120	99.975	± 0.016	Penn State
	trans-1,2-Dimethylcyclopentane	138	99.87	± 0.10	Penn State
	trans-1,3-Dimethylcyclopentane	102	99.65	± 0.09	APIRP45
C_8H_{16}	n-Propylcyclopentane	350	99.81	± 0.10	APIRP45
	Isopropylcyclopentane	370	99.81	± 0.07	APIRP45
	1-Methyl-1-ethylcyclopentane	370	99.91	± 0.08	Penn State
	cis-1-Methyl-2-ethylcyclopentane	158	99.71	± 0.24	Penn State
	1,1,2-Trimethylcyclopentane	115	99.988	± 0.009	Penn State
	1,1,3-Trimethylcyclopentane	65	99.56	± 0.32	APIRP45; Gulf-Mellon
	cis,cis,cis-1,2,3-Trimethylcyclopentane	100	99.93	± 0.06	Penn State
	cis,trans,cis-1,2,3-Trimethylcyclopentane	50	99.92	± 0.04	Penn State
	cis,cis,trans-1,2,4-Trimethylcyclopentane	81	99.65	± 0.23	Penn State
	cis,trans,cis-1,2,4-Trimethylcyclopentane	125	99.79	± 0.10	Penn State
	n-Butylcyclopentane	345	99.970	± 0.025	APIRP45
	Isobutylcyclopentane	290	99.88	± 0.08	APIRP45
	Alkylcyclohexanes				
C_6H_{12}	Cyclohexane	400	99.997	± 0.002	Barrett
C_7H_{14}	Methylcyclohexane	400	99.90	± 0.08	Barrett; APIRP45
C_8H_{16}	Ethylcyclohexane	450	99.90	± 0.08	APIRP45
	1,1-Dimethylcyclohexane	131	99.93	± 0.03	APIRP45
	cis-1,2-Dimethylcyclohexane	243	99.983	± 0.015	APIRP45
	trans-1,2-Dimethylcyclohexane	330	99.92	± 0.07	APIRP45
	cis-1,3-Dimethylcyclohexane[l]	360	99.94	± 0.05	APIRP45
	trans-1,3-Dimethylcyclohexane[m]	360	99.88	± 0.07	APIRP45
	cis-1,4-Dimethylcyclohexane	215	99.94	± 0.04	Std. Oil Dev.
	trans-1,4-Dimethylcyclohexane	260	99.89	± 0.08	Std. Oil Dev.
C_9H_{18}	n-Propylcyclohexane	360	99.94	± 0.05	APIRP45
	Isopropylcyclohexane	147	99.90	± 0.07	APIRP45
	1,1,3-Trimethylcyclohexane	199	99.85	± 0.05	APIRP45
$C_{10}H_{20}$	n-Butylcyclohexane	215	99.958	± 0.039	APIRP45
	Isobutylcyclohexane	200	99.85	± 0.09	APIRP45
	sec-Butylcyclohexane	210	(99.75	± 0.20)[e]	APIRP45
	tert-Butylcyclohexane	285	99.96	± 0.03	APIRP45
	Mono-olefins				
C_5H_{10}	1-Pentene (A)	195	99.34	± 0.40[n]	Phillips
	1-Pentene (B)	470	99.82	± 0.12	Phillips
	cis-2-Pentene (A)	82	99.80	± 0.15	APIRP45
	trans-2-Pentene	367	99.93	± 0.05	APIRP45
	2-Methyl-1-butene (A)	450	99.89	± 0.08	General Motors
	3-Methyl-1-butene	88	99.78	± 0.12	Houdry
	2-Methyl-2-butene	530	99.945	± 0.046	General Motors
C_6H_{12}	1-Hexene	545	99.87	± 0.08	APIRP45
	trans-2-Hexene	350	99.84	± 0.11	APIRP45
	trans-3-Hexene	200	99.95	± 0.03	APIRP45
	2-Ethyl-1-butene	280	99.95	± 0.04	APIRP45; APIRP6[d]
	3,3-Dimethyl-1-butene	385	99.91	± 0.06	Penn State
C_7H_{14}	1-Heptene	220	99.84	± 0.10	APIRP45
C_8H_{16}	1-Octene	600	99.77	± 0.13	APIRP6[d]
	Diolefins				
C_4H_6	1,2-Butadiene	100	99.94	± 0.05	Std. Oil Dev.
	Acetylenes				
C_4H_6	1-Butyne (ethylacetylene)	265	99.90	± 0.07	APIRP45
	2-Butyne (dimethylacetylene)	265	99.959	± 0.038	APIRP45
	Cyclomono-olefins				
C_5H_8	Cyclopentene	240	99.975	± 0.021	Atlantic: APIRP45
C_6H_{10}	Cyclohexene	735	99.978	± 0.020	APIRP6[d]

but will normally affect the freezing point appreciably; (c) in a series of fractions obtained from a distillation at high efficiency of a hydrocarbon containing close-boiling isomers as impurity, the fractions of highest* purity will be beyond or ahead of the middle portion of the distillate as frequently as in the middle portion; (d) for producing material of highest purity, the fractions of distillate can be blended safely only on the basis of the freezing points of selected fractions. An example of a case where the purest material is near the beginning of a distillation is shown in Figure 3, for 2,2-dimethylhexane, and an example of a case where the purest material is at the very end of the distillation is shown in Figure 4, for cis-2-pentene.

In the four years ending June 30, 1947, in the cooperative work with the American Petroleum Institute, there have been produced a total of 120 pure hydrocarbon compounds, including normal paraffins, isoparaffins, cyclopentane and its alkyl derivatives, cyclohexane and its alkyl derivatives, benzene and its alkyl derivatives, mono-olefins, diolefins, acetylenes, and cyclomono-olefins (5, 15, 16, 17). Table II lists these 120 compounds completed as of June 30, 1947, and gives the volume of the A.P.I.–N.B.S. sample prepared and the name of the laboratory which supplied the starting material. (Samples of these compounds are made available on loan to qualified investigators for the measurement of needed properties, by the Advisory Committee for the A.P.I. Research Project 44 at the National Bureau of Standards.) With the exception of ethylcyclo-

[l] This isomer, formerly labeled trans, has following properties: boiling point at 1 atm., 120.09° C.; refractive index, n_D at 25° C., 1.4206; density at 25° C., 0.7620 g. per ml. American Petroleum Institute Research Project 44 at National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table 7a.

[m] This isomer, formerly labeled cis, has following properties: boiling point at 1 atm., 124.45° C.; refractive index, n_D at 25° C., 1.4284; density, at 25° C., 0.7806 g. per ml. American Petroleum Institute Research Project 44 at National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table 7a.

[n] Revised; originally reported as 99.49 ± 0.40.

butane, all these compounds are available, in the same or slightly less purity, as N.B.S. standard samples (10, 11), and may be purchased through the American Petroleum Institute by laboratories in the petroleum industry in the United States and through the National Bureau of Standards by all other laboratories.

DETERMINATION OF PURITY BY MEASUREMENT OF FREEZING POINTS

As has been indicated, one of the most effective tools for evaluating the purity of chemical substances is that involving determination of the freezing point. In connection with the work on hydrocarbons at the National Bureau of Standards, the freezing point, with suitable observation of the temperature of the liquid-solid equilibrium as a function of the fraction of the sample frozen or melted, has for many years been used to determine the purity of hydrocarbons.
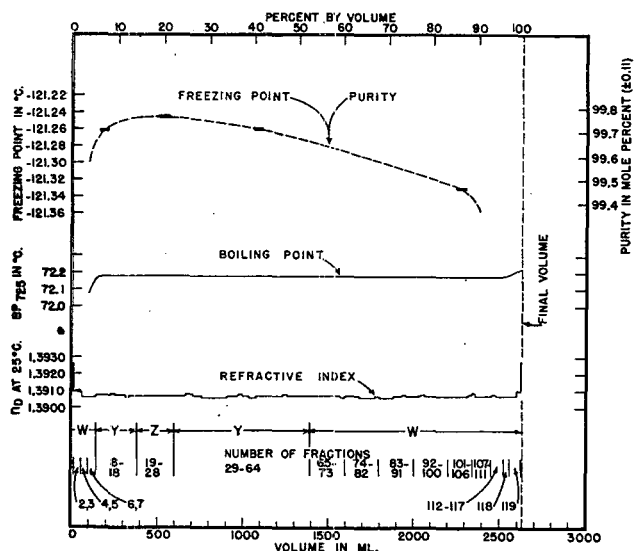

Figure 3.   Results of Second and Final Distillation of 2,2-Dimethylhexane

Azeotropic distillation with ethanol at 725 mm. of mercury.   Still 13 (1/9/45 to 2/7/45)

For the equilibrium between a crystalline phase consisting of the major component alone and a liquid phase consisting of the major component and one or more other components, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase, for an ideal or sufficiently dilute solution, is (6, 18):

$$-\ln N_1 = -\ln (1 - N_2) = (\Delta H_{f_0}/RT_{f_0}^2)\ (t_{f_0} - t) \times$$
$$[1 + (1/T_{f_0} - \Delta C_{p_0}/2 \Delta H_{f_0})\ (t_{f_0} - t) + \ldots] \quad (1)$$

where

N_1 = mole fraction of major component in liquid phase
N_2 = $(1 - N_1)$ = sum of mole fractions of all other components in liquid phase
t_{f_0} = temperature, in ° C., of freezing point of major component when pure—that is, when $N_2 = 0$
t = given temperature of equilibrium, in ° C.
R = gas constant, per mole
T_{f_0} = $t_{f_0} + 273.16$
ΔH_{f_0} = heat of fusion per mole, of major component in pure state at temperature T_{f_0}
ΔC_{P_0} = heat capacity per mole, of pure liquid less that of pure solid, for major component in pure state at temperature T_{f_0}

It is seen that the three constant terms (t_{f_0}), $(\Delta H_{f_0}/RT_{f_0}^2)$, and $(1/T_{f_0} - \Delta C_{p_0}/2\ \Delta H_{f_0})$, in Equation 1 are properties of the major component only, so that the relation between the tempera-

ture of equilibrium and the mole fraction of solute is the same for all solutes, provided they remain in the liquid phase and form with the major component an ideal solution.

In those cases where significant departures from the ideal solution law occur, but where the addition of solute to the pure solvent still lowers the freezing point of the solvent, the relation between the temperature of the solid-liquid equilibrium and the composition of the liquid phase can be expressed, in the dilute region, by an equation of the form of Equation 1:

$$-\ln N_1 = -\ln (1 - N_2) = A\ (t_{f_0} - t_f)\ [1 + B\ (t_{f_0} - t_f) + \ldots] \quad (2)$$

The constants A and B in Equation 2 are determined experimentally for given systems by measuring the lowering of the freezing point of the major component on the addition of known amounts of known impurities (solutes). In Equation 2, constant A has replaced in Equation 1 the term $(\Delta H_{f_0}/RT_{f_0}^2)$ and B has replaced the term $(1/T_{f_0} - \Delta C_{p_0}/2 \Delta H_{f_0})$.

If r is the fraction crystallized of the total number of moles of all components in the system, then

$$t = t_{f_0} - a/[\{1 - (b/a)\} - r] \quad (3)$$

where a and b are constants for the given sample. Equation 3 gives the relation between the temperature of equilibrium and the fraction of material crystallized (18).

When the experiment is performed according to the procedure followed in this laboratory, involving time-temperature freezing and melting experiments, the rate of crystallization or melting of the major component is substantially constant with time, and

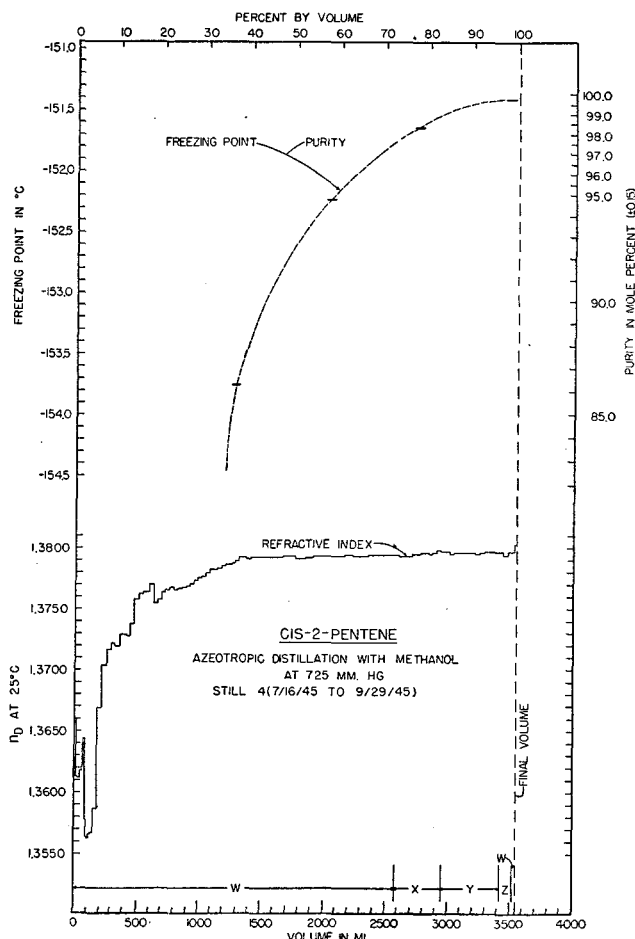$$r = k\ (z - z_f) \quad (4)$$

Figure 4.   Results of First and Only Distillation of cis-2-Pentene

Azeotropic distillation with methanol at 725 mm. of mercury.   Still 4 (7/16/45 to 9/29/45)
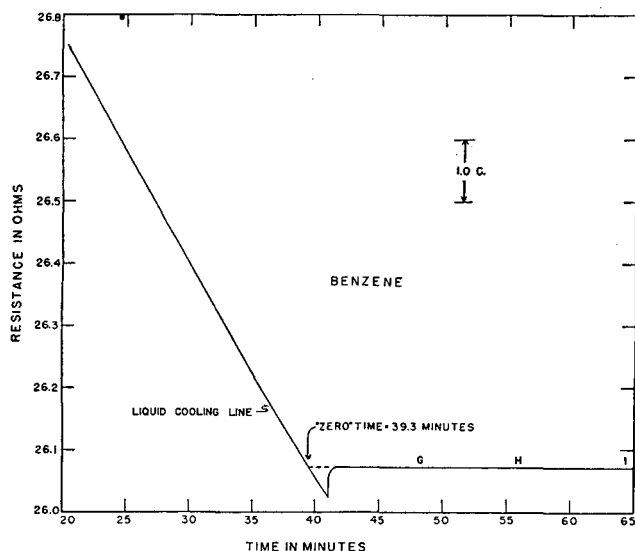
Figure 5. Time-Temperature Cooling Curve for Determining Zero Time in an Experiment on a Sample of Benzene

Scale of ordinates gives resistance in ohms of platinum resistance thermometer, and scale of abscissas gives time in minutes. *GHI* represents equilibrium portion of freezing curve. Zero time is given by intersection of liquid cooling line with *GHI* extended. Same data plotted in Figure 6 with a magnified scale of temperature

where k is a constant characteristic of the given experiment, z is any given time, and z_f is the time at which freezing begins or melting is complete. Combination of Equations 3 and 4 yields

$$t = t_{f_0} - a'/[1 - k'(z - z_f)] \qquad (5)$$

where a' and k' are constants. Equation 5 gives the relation between the temperature of equilibrium and the time during the part of the experiment in which equilibrium between the liquid and solid phases of the major component exists (*18*).

Equation 1, relating temperature and the composition of the liquid phase in the solid-liquid equilibrium in an ideal system, involves the two assumptions that all of the solute impurities remain in the liquid phase during crystallization and form with the·major component a substantially ideal solution. The first assumption requires the absence of mixed crystals. The tendency to form mixed crystals is more favorable when the solute molecules have nearly the same size and shape as do the molecules of the major component, permitting some of the latter molecules in the crystalline lattice to be replaced by solute molecules without fusion of the crystal. This replacement of molecules of the major component in the crystalline lattice by appropriate solute molecules without fusion of the crystal is further made much more favorable in the case where the crystalline form of the major component is the product of a transition below the freezing point associated with the absorption of a quantity of energy comparable to the energy of fusion. In such case, the crystal, which has a small heat of fusion, is not far removed from the liquid state and possesses considerable mobility of structure, thus permitting greater latitude in the size and shape of the solute molecules which may enter the crystalline lattice without its actual fusion—the formation of mixed crystals may be suspected in any system in which the major component has a small heat of fusion.

Fortunately, in the case of hydrocarbons of low molecular weight, mixed crystals occur only seldom between a given hydrocarbon and the other hydrocarbons which are likely to remain as impurity in the given hydrocarbon after the latter has been subjected to a thorough fractionation, except in the above-mentioned cases involving a major component of small heat of fusion. Furthermore, with regard to the assumption requiring that the impurity form with the major component a substantially ideal solution, it is apparent that when a given hydrocarbon has been

put through a logical system of purification there will remain as impurity only those hydrocarbons which are very similar to the major component. These latter hydrocarbons are, however, precisely those which are most likely to form with the major component a substantially ideal solution.

For calculating the purity of a given compound from measurement of the freezing point, it is convenient to transform Equation 2 to the following form:

$$\log_{10} p = 2.00000 - (A/2.30259)(t_{f_0} - t_f)[1 + B(t_{f_0} - t_f)] \quad \cdot (6)$$

In Equation 6, p is the purity in mole per cent; t_f is the freezing point of the given sample under specified conditions, as in air at 1 atmosphere; t_{f_0} is the value of the freezing point for zero impurity, for the same specified conditions; and A and B are the first and second cryoscopic constants already defined.

As described above, cryoscopic constants A and B are evaluated for the ideal case from values of the freezing point, heat of fusion, and heat capacity of liquid and solid of the major component, and, for the cases where significant departures from the ideal solution law occur, A and B are evaluated from measurements of the lowering of the freezing point of the major component on the addition of known amounts of the appropriate known solute impurities.

In this laboratory, the value of the freezing point for zero impurity is.usually determined from observations on the purest sample of the material available, utilizing time-temperature freezing or melting curves of the kind described in this report (*6, 18*). If equipment, time, and personnel are available, calorimetric observations of the kind described by Huffman (*7*) may be utilized to obtain even more accurate values.

In this laboratory, the freezing point is determined by means of time-temperature freezing and melting curves obtained with an apparatus including a precision platinum resistance thermometer (*6*).
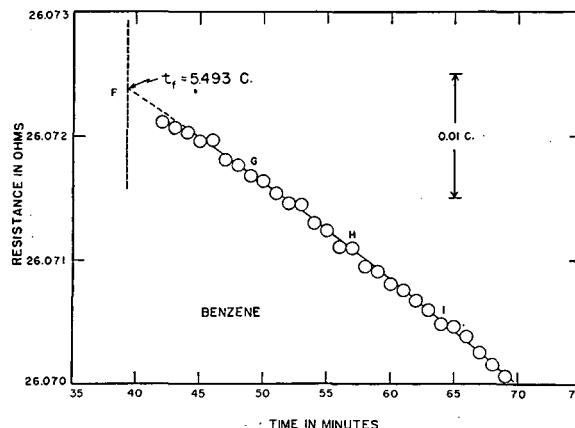
Figure 6. Time-Temperature Cooling Curve for Determining Freezing Point of a Sample of Benzene of Purity 99.4 mole %

Scale of ordinates gives resistance in ohms of platinum resistance thermometer, and scale of abscissas gives time in minutes. *GHI* represents equilibrium portion of freezing curve. Freezing point *F* is obtained by geometrical extrapolation of equilibrium portion of curve. Same data as plotted in Figure 5

About 50 ml. of the hydrocarbon to be examined are placed in an inner vacuum flask. The hydrocarbon is stirred by a stirrer which is operated longitudinally by the motor overhead. The platinum resistant thermometer is located near the bottom center of the inner flask. An outer vacuum flask contains the refrigerant for cooling. Observations of time and temperature are made, starting with the liquid above the freezing point and continuing until the stirrer begins laboring. The time-temperature observations are plotted to obtain the proper value of the freezing point, as shown in Figures 5 and 6 for a sample of benzene (*6*). Figure 5, having a compressed scale of resistance (or temperature), is used to determine the "zero" time, at which crystallization would have begun in the absence of undercooling. In Fig-

ure 6, the points marked *GHI* identify the equilibrium portion used to determine by geometrical extrapolation the proper value of the freezing point at *F* (*6*).

Some substances, such as ethylbenzene, normally do not yield equilibrium time-temperature freezing curves. For such compounds, the determination of the freezing point is made from melting curves, samples of which are shown in Figures 7 and 8 (*6*). In performing melting experiments, the procedure is the

same as in the freezing experiments, except that at the time the stirrer begins laboring the cooling bath is replaced by an appropriate warming bath (for ethylbenzene, a slurry of solid carbon dioxide in equal volumes of carbon tetrachloride and chloroform is suitable). As before, Figure 7 is used to determine "zero" time and Figure 8 is used to determine the freezing point at *F*, with points *GHI* identifying the equilibrium portion of the curve. Figure 9 shows, with both the compressed and expanded scale of resistance (temperature), the results of a typical time-temperature melting experiment on 2-methyl-1-butene (*5*). In each case, the equilibrium portion of the curve (*GHI*) is extrapolated by a geometrical procedure (*18*) to the time at which, in the freezing experiment, crystallization would have just begun in the absence of undercooling, or at which, in the melting experiment, all the crystals would have just melted if no departure from equilibrium occurred as the amount of crystals diminished to near zero (*18*).

In the case of substances which crystallize readily and have a normal heat of fusion, as, for example 1,3-butadiene, the freezing point of the same sample can be reproduced repeatedly within ±0.003° C. from time-temperature freezing experiments.

For hydrocarbons having normal heats of fusion, it is surprising how closely the most probable impurities usually follow the ideal solution laws relating the composition of the liquid phase with the temperature of the liquid-solid equilibrium. At the National Bureau of Standards, a considerable amount of data have been obtained on this point in investigations for the Office of Rubber Reserve on the determination of purity by measurement of freezing points of compounds involved in the production of synthetic rubber, specifically 1,3-butadiene, isoprene, and styrene (*4*). In the case of 1,3-butadiene, it was found that the addition,

Figure 7. Time-Temperature Warming Curve for Determining Zero Time in an Experiment on a Sample of Ethylbenzene

Scale of ordinates gives resistance in ohms of platinum resistance thermometer, and scale of abscissas gives time in minutes. *HG* represents part of equilibrium portion of warming curve. Zero time is given by intersection of *HG* extended to intersection with backward extension of liquid warming line. Same data plotted in Figure 8 with a magnified scale of temperature
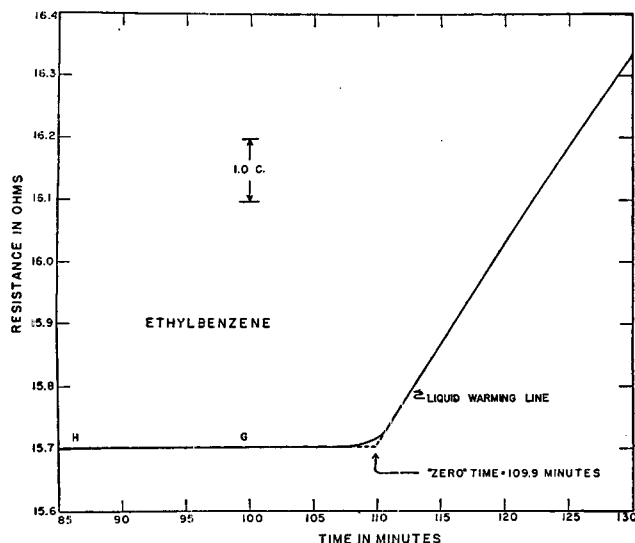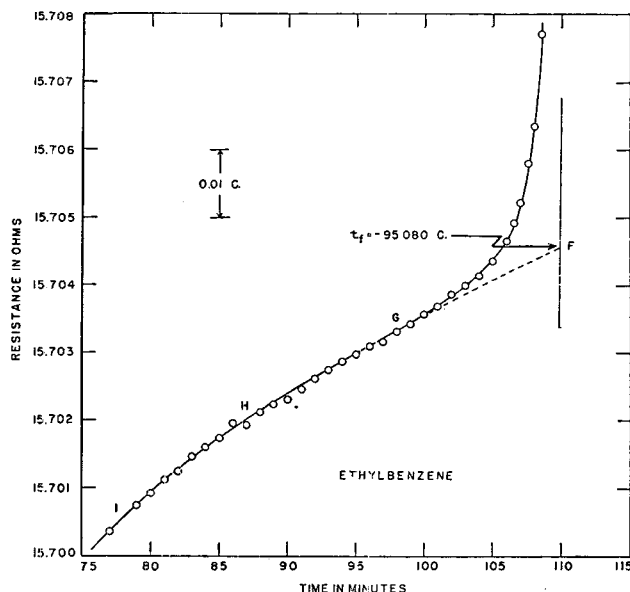
Figure 8. Time-Temperature Warming Curve for Determining Freezing Point of a Sample of Ethylbenzene Having a Purity of 99.64 Mole %

Scale of ordinates gives resistance in ohms of platinum resistance thermometer, and scale of abscissas gives time in minutes. *IHG* represents equilibrium portion of melting curve. Freezing point is obtained by geometrical extrapolation of *IHG*. Same data as plotted in Figure 7

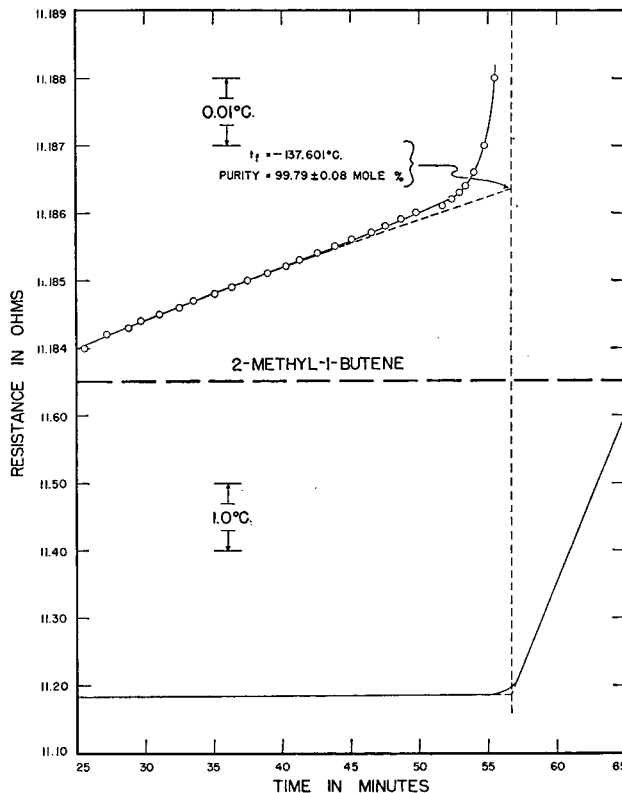**Figure 9. Time-Temperature Warming Curves for Determining Freezing Point of a Sample of 2-Methyl-1-butene**

Scale of ordinates gives resistance in ohms of platinum resistance thermometer (0.1 ohm is approximately 1.0° C.). Scale of abscissas gives time in minutes. Same data are used for both curves, but scale of temperature (or resistance) for upper curve is magnified 100 times that for lower curve

up to about 6 mole %, of known amounts of the following solutes as impurities produced lowerings of the freezing point in accord with the ideal solution law within the limits of uncertainty: 1-butene, cis-2-butene, trans-2-butene, isobutene, 1,2-butadiene, styrene, and 4-vinyl-1-cyclohexene. Similarly, in the case of isoprene, the addition, up to about 5 mole %, of known amounts of the following solutes as impurities yielded ideal values of the lowering of the freezing point: n-pentane, 1-pentene, trans-2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, cis-1,3-pentadiene, trans-1,3-pentadiene, and dimethylacetylene. In the case of styrene, the addition, up to about 6 mole %, of known amounts of the following solutes as impurities yielded ideal values of the lowering of the freezing point: benzene, o-xylene, m-xylene, n-propylbenzene, isopropylbenzene, and 4-vinyl-1-cyclohexene. On the other hand, in the case of styrene, ethylbenzene, and toluene it yielded values of the lowering of the freezing point about 10% less than those called for by the ideal solution law, over the same range of composition.

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[End of Symposium on Purity and Identity]

Systematic Multiple Fractional Extraction Procedures

Principles of Application to Separation of (Organic) Mixtures

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The analysis of mixtures of (organic) substances by means of discontinuous multiple fractional extractions is discussed. The assumptions underlying the method are stated. A simple mathematical treatment is developed which, in conjunction with the calculated data and graphs, will be of aid in the application of this method to practical problems in the laboratory. For a mixture of two substances having partition constants K_a and K_b, the greatest fractional separation for a given number of extractions is attained if the ratio of the volumes of the two solvents, X and Y, is maintained at

$$V_x/V_y = \sqrt{\frac{1}{K_a K_b}}$$

and the extractions are carried out according to a procedure similar to that described by Jantzen. The application of the method to the examination of unknown mixtures, to the search for known compounds in unknown mixtures, to the quantitative analysis of qualitatively known mixtures and to the testing of "pure" substances for homogeneity is discussed.

DURING the past ten years in this laboratory, studies of the metabolic fate of barbituric acid anesthetics have led to the development of systematic fractional extraction procedures for the isolation of these and related substances from urine and tissues. These procedures are applicable in a perfectly general way to similar studies of most drugs, and to the separation of many naturally occurring and synthetic mixtures of organic compounds.

The studies recently reported by Craig and co-workers (7-13, 25) appear to be the only ones in which the method is developed adequately for general application in the laboratory. By means of his countercurrent distribution machine Craig can subject a few hundred milligrams more or less of material to a large num-

ber of fractional extractions (200 or more) in a precise systematic way. He is thus able to test the homogeneity of a substance much more rigorously than has been common practice.

The studies described here have been made along somewhat different lines, usually directed towards the isolation of known substances from (or the estimation of an upper limit to the amount present in) complex biological mixtures, or the separation of unknown substances which can be assayed biologically. This development of the method includes most of the steps which are necessary preliminaries to the application of Craig's machine, but it also includes useful variations on the latter method of separation and of investigation of homogeneity.

The theory of multiple fractional extraction (discontinuous) has been discussed in detail particularly by Jantzen (16) and by Hunter and Nash (14). Continuous countercurrent extraction has been

studied particularly by Varteressian and Fenske (*24*), Cornish *et al.* (*6*), and Martin and Synge (*17*). A special case of the latter, the now well-known "partition chromatography," was developed by Martin and Synge (*18*). The mathematical treatments of the subject by all these authors are extensive. The following mathematical treatment is comparatively naive; yet it seems to describe discontinuous batch operations adequately, and it may therefore be found useful—particularly in organic and biological laboratories.

The purposes of the present paper are: to restate the basic assumptions and definitions underlying this method of analysis, to derive simple algebraic relationships which will be useful in the application of the method, and to discuss the adjustment of the volume ratio of the two solvents as a means of achieving the maximum separating power of the procedure in each case.

THEORETICAL

For the development of simple "distribution curves" the usual definitions and assumptions are made:

1. A pure substance (relatively nonvolatile, nonreacting) in solution can be distributed between two immiscible liquid phases, X and Y, such that at equilibrium

$$\frac{\text{Mg. of } A \text{ per cc. of } X}{\text{Mg. of } A \text{ per cc. of } Y} = K_a \qquad (1)$$

The "distribution coefficient" or "partition constant," K_a, is known to vary somewhat with concentration in most cases. It is, therefore, important to state the actual experimental ratio(s) of concentrations from which a certain K is derived. It is assumed, however, that concentration ranges where K does not vary appreciably (dilute solutions) can be used. At any stage in an experiment this can be checked precisely.

2. For present purposes it is assumed that the solutes under consideration are neither associated nor dissociated appreciably in either solvent. In practice, by use of dilute solutions and certain other maneuvers the effects of these processes can usually be controlled.

3. The conditions of equilibrium (such as composition of solvents, temperature) are constant.

4. There is only negligible adsorption of solute on the apparatus or at the liquid-liquid interface. This adsorption may be an important factor in the cases of certain very dilute solutions. Analysis of (portions of) both phases and comparison of the sum with the initial total amount of solute will show whether this occurs.

If the total volumes of the two solvents are designated as V_x and V_y, respectively, and p_a represents the fraction of solute A which is in solvent X at equilibrium ($1 - p_a$, the remainder of A, is in solvent Y), then

Total amount of A in $X =$
$$\text{(mg. per cc. of } X)V_x \qquad (2)$$

Total amount of A in $Y =$
$$\text{(mg. per cc. of } Y)V_y \qquad (3)$$

and

$$\frac{p_a}{1 - p_a} = \frac{\text{(mg. per cc. of } X)V_x}{\text{(mg. per cc. of } Y)V_y} = \frac{K_a V_x}{V_y} \qquad (4)$$

By transposing and combining appropriate terms of Equation 4

$$p_a = \frac{K_a V_x}{K_a V_x + V_y} \qquad (5)$$

In the following discussion the fraction of solute A in solvent Y will be called q_a such that $q_a = 1 - p_a$, or $p_a + q_a = 1$.

5. In dealing with mixtures of solutes it is assumed that each solute distributes independently. Since in practice this is likely to be erroneous for concentrated solutions, it is desirable to work with reasonably dilute solutions—usually below 10 mg. per cc. and sometimes below 1 mg. per cc. at the start of the extractions.

Calculation of Distribution of Solute. The calculation of the distribution of each solute of a mixture can be made (algebraically) on the basis of Equation 5, for each single equilibration or "shake" in a separatory funnel or test tube. In Figure 1, $X I_0$ and $Y I_0$ are the initial portions of the respective solvents (previously mutually saturated) into one or both of which the solute is introduced. On separation the two equilibrated solutions are designated as $X I_1$ and $Y I_1$ where the subscript denotes the number of extractions through which the solution has passed. A systematic multiple fractional extraction is developed (*16*) by introducing fresh portions of both solvents ($X II_0$, $X III_0$, etc., and $Y II_0$, $Y III_0$, etc., volumes equal to those of $X I_0$ and $Y I_0$, respectively) and continuing the extractions according to the scheme in Figure 1, using additional separatory funnels or test tubes as needed.

The algebraic calculation of the fraction of a solute in each of these solutions can readily be carried out as indicated in Figure 1, where (1) the combinations and separations are carried out as directed by the arrows, (2) the circled terms represent the fractional amounts of a single solute combined and equilibrated between the two phases in a separatory funnel; (3) to obtain the two terms below an equilibration, add the two terms above
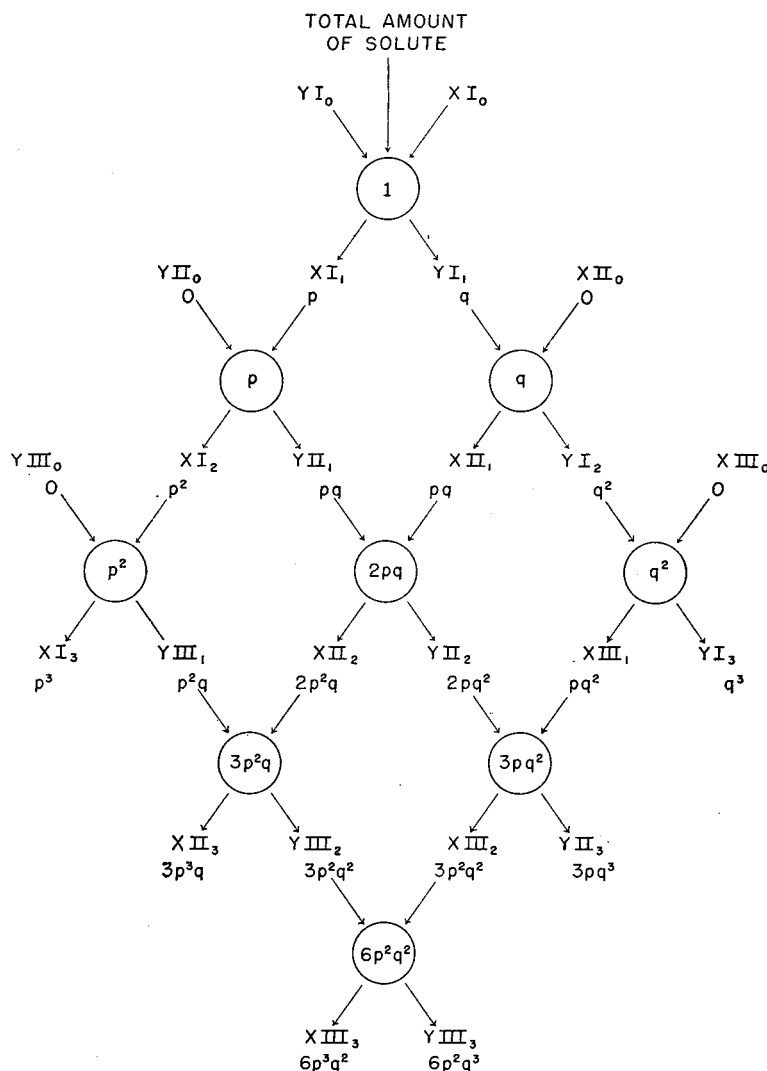

Figure 1. Distribution of Solute between Immiscible Solvents X and Y

the equilibration (the sums are in the circles), and multiply by p for the X term below and by q for the Y term below.

If n equals the number of portions of each solvent used, then the process is carried through the stage $n = 3$ in Figure 1; the actual number of extractions performed is n^2; the total number of fractions after completion of the extractions is $2\,n$.

For continuation to higher values of n the procedure is simple and Figure 2 shows the terms up to $n = 6$. The composition of every phase is defined in terms of p and q. By appropriate combination of terms of horizontal lines through p^n the terms of the binomial expansion of $(p + q)^n$ are obtained. These terms represent the total solute content of the two phases in a separatory funnel at that stage (Craig, 8).

In the diamond-shaped arrangement shown in Figures 1 and 2 the procedure is carried through a "diagonal stage." There are three practical reasons for continuing until this stage is reached rather than stopping at a "horizontal stage." (1) Two solutes can be separated in such a way that most of one will accumulate in one solvent and most of the other will accumulate in the other solvent. (2) A particular solute can be made to accumulate in the desired solvent. (3) This stage represents the maximum

accomplishment which it is convenient to make with n separatory funnels and n batches of each solvent.

The subsequent discussions in this paper are generally in terms of such "diagonal stages," where each of the first n terms represents, respectively, the fraction of solute in each of the n batches of solution in solvent X and (going up the other bottomside of the diamond) the next n terms represent the fractions of the solute in the n batches of solution in solvent Y, in reverse order.

For the calculation of the terms of the nth diagonals (the diagonals the first terms of which are p^n and q^n) the following equation can be used:

$$1 = p^n + \frac{n!}{(n-1)!}\,p^n q + \frac{(n+1)!}{2!(n-1)!}\,p^n q^2 + \frac{(n+2)!}{3!(n-1)!}\,p^n q^3 + \ \cdot \ \cdot \ \cdot$$

$$\frac{(2n-2)!}{(n-1)!(n-1)!}\,p^n q^{n-1} + \text{same series with } p \text{ and } q \text{ interchanged}$$
$$\text{and the terms in reverse order} \quad (6)$$

The first (or last) term of this expansion (or of the binomial expansion) was given by Hunter and Nash (14, page 839) in terms similar to those employed here.

If it is desired to plot the data, these diagonal values can give general pictures similar to those obtained by Craig. In Table I
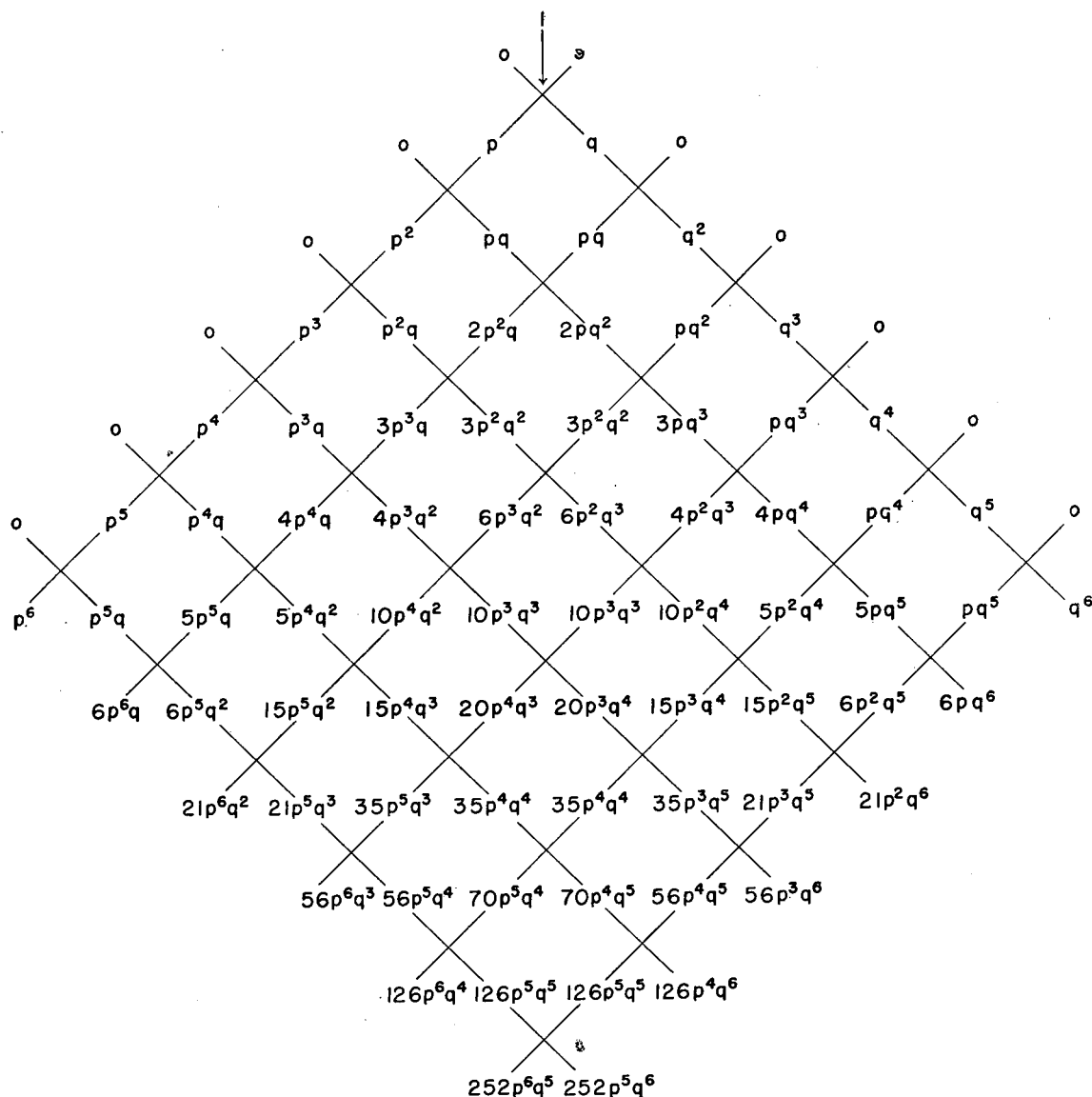

Figure 2.   The Expansion of Figure 1 Carried through $n = 6$

Table I. Numerical Data for Sixth Diagonals of Figure 2

	$X\,I_6$	$X\,II_6$	$X\,III_6$	$X\,IV_6$	$X\,V_6$	$X\,VI_6$	$Y\,VI_6$	$Y\,V_6$	$Y\,IV_6$	$Y\,III_6$	$Y\,II_6$	$Y\,I_6$
No.	1	2	3	4	5	6	7	8	9	10	11	12
p	p^6	$6p^5q$	$21p^3q^2$	$56p^6q^3$	$126p^6q^4$	$252p^5q^5$	$252p^5q^6$	$126p^4q^6$	$56p^3q^6$	$21p^2q^6$	$6pq^6$	q^6
0.1	0.0_51	0.0_454	0.0_417	0.0_441	0.0_483	0.0_315	0.0013	0.0067	0.0297	0.1113	0.3189	0.5314
0.2	0.0_464	0.0_331	0.0_386	0.0018	0.0033	0.0054	0.0203	0.0528	0.1174	0.2202	0.3146	0.2621
0.25	0.0_324	0.0011	0.0029	0.0058	0.0097	0.0146	0.0438	0.0876	0.1557	0.2336	0.2670	0.1780
0.3	0.0_373	0.0030	0.0075	0.0140	0.0205	0.0309	0.0721	0.1200	0.1780	0.2222	0.2118	0.1176
0.35	0.0018	0.0072	0.0163	0.0283	0.0414	0.0538	0.0998	0.1426	0.1811	0.1940	0.1584	0.0754
0.4	0.0041	0.0144	0.0310	0.0495	0.0666	0.0802	0.1205	0.1507	0.1672	0.1568	0.1120	0.0467
0.45	0.0083	0.0274	0.0527	0.0773	0.0957	0.1054	0.1289	0.1430	0.1413	0.1179	0.0747	0.0277
0.49	0.0138	0.0424	0.0755	0.1028	0.1180	0.1204	0.1253	0.1279	0.1159	0.0887	0.0517	0.0176
0.50	0.0156	0.0468	0.0820	0.1095	0.1231	0.1231	....	....	....	....	....	....

are given numerical data calculated from the twelve terms of the sixth diagonals of Figure 2 for various values of p. For $p > 0.5$ read from right to left along the proper line (reverse p and q). Figure 3 shows the data of Table I plotted in such a way that the fractional amount of solute in each of the twelve batches of solution can be estimated for any value of p. Figure 4 gives similar data for $n = 10$. Figure 5 shows curves of distribution of solute for certain values of p, plotted according to the method of Craig (8).

Separation of Mixtures. In dealing with separations of mixtures of two components (A and B, distribution coefficients K_a and K_b) the question arises: What volume ratio of the two solvents should be used? This, of course, depends upon the end desired. In the early work in this laboratory it soon became clear that to get each solute reasonably well separated from the other, it is usually advantageous to use some volume ratio other than 1. Long ago (4) it was guessed from empirical considerations that the desired result would be obtained by adjusting V_x/V_y such that the fraction of solute A in solution $X\,I_1$ is equal to the fraction of solute B in solution $Y\,I_1$.

This condition can be represented algebraically by proper substitutions in Equation 5:

$$\frac{K_a V_x}{K_a V_x + V_y} = 1 - \frac{K_b V_x}{K_b V_x + V_y} \qquad (7)$$

which can be simplified to

$$\frac{V_x}{V_y} = \sqrt{\frac{1}{K_a K_b}} \qquad (8)$$

The separation of two-component or multicomponent mixtures can readily be studied by the use of tables such as Table I, and sets of curves such as Figures 3, 4, and 5. Examination of Table I and of Figure 5 reveals that for each value of p the curve of distribution of a single solute passes through a maximum. If the volume ratio be adjusted according to Equation 8 the distribution curves of the two solutes will be mirror images of each other. For example, if $K_a = 4.0$ and $K_b = 0.25$ (16), Equation 8 gives $V_x/V_y = 1$; from Equation 5 then, $p_a = 0.80$ and $p_b = 0.20$. The distribution curve for p_b is read from Table I, and that for p_a is the same but with p and q reversed (read from right to left along the line $p = 0.2$). In a similar manner, for $K_a = 1.50$ and $K_b = 3.38$, $V_x/V_y = 0.444$, $p_a = 0.40$, and $p_b = 0.60$ (Figure 5).

The full significance of the adjustment of the volume ratio according to Equation 8 was not realized until careful studies were made of the "fractional separation" of various pairs of substances with various volume ratios. In Figure 5 are plotted two typical pairs of curves which show the effect of variation of V_x/V_y on the distribution of substance A ($K_a = 2.25$) and of substance B ($K_b = 1.0$). In order to make comparisons of such "symmetrical" ($p_a = q_b$) and "unsymmetrical" ($p_a \neq q_b$) separations, a definition of "fractional separation," S, of A and B can be made as follows:

$$S = 1 - \frac{1}{2}\left(\begin{array}{l}\text{sum of fractions of }A\text{ to right of intersection of}\\ \text{the two curves + sum of fractions of }B\text{ to left of}\\ \text{intersection of the two curves}\end{array}\right)$$

It is also true within the limits of the accuracy of measurement that:

$$S = 1 - \frac{1}{2}\left(\frac{\text{area common to the intersecting curves}}{\text{total area under one whole curve}}\right)$$

although this replaces a discontinuous function with a continuous one.

Martin and Synge (18) have used area ratios in a different way to correlate "degree of separation" with a function of the two partition constants and the "number of plates." This function of the two partition constants seems to be $K_a p_b / K_b p_a$ (substituting V_y and V_x, respectively, for A_L and A_S of Martin and Synge). Their Figure 2 (18, page 1362) appears to be related to Figure 8.

The area under one whole curve is independent of the value of p, but the area common to the intersecting curves is a function of the relationship between p_a and p_b, which in turn is a function of V_x/V_y (for given K_a and K_b). For the example of Figure 5,

$$S = 1 - \frac{(18.8 + 18.8)\ \text{cm.}^2}{2 \times 98.5\ \text{cm.}^2} = 1 - 0.191 = 0.809$$
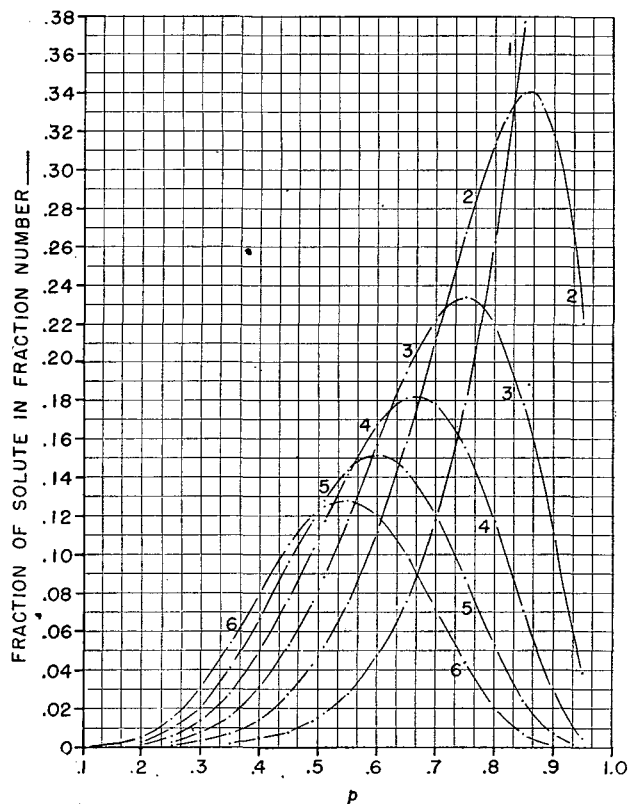

Figure 3. Fractions of Solute in Twelve Fractions for $n = 6$ and All Values of p

Numerical data from Table I. To find values "fraction of solute" in fractions 7, 8, 9, etc., for a given p, find $1 - p$ on abscissa and opposite this find the sought values on curves 6, 5, 4, etc.

when $\dfrac{V_x}{V_y}$ is adjusted to give $p_a = 0.6$ and $p_b = 0.4$. For volume ratio 1, $p_a = 0.693$, $p_b = 0.500$, and

$$S = 1 - \frac{(24.2 + 17.2)\text{ cm.}^2}{197\text{ cm.}^2} = 0.800$$

Similar measurements for other pairs of K's can be shown by curves such as those of Figure 6. These show that for a given

pair of K's and a given value of n the "fractional separation" is a maximum for V_x/V_y adjusted according to Equation 8.

By comparison of the numerically calculated values it can be shown that the difference between S for V_x/V_y adjusted according to Equation 8 and S for some other V_x/V_y becomes greater as n is increased (for $S <$ about 0.9). For small ratios of the two K's and small increase of n these differences are too small to show on the graph (Figure 6).

It can also be shown by comparison of appropriate areas, or by calculating S numerically, that the cutting of the total number of fractions into two batches as indicated by perpendicular dotted lines passing through the intersection of the distribution curves (Figure 5) (pooling the first seven batches in solvent X for the example of $p_a = 0.693$, $p_b = 0.500$) gives a greater value of S than cutting between any other pair of fractions.

This concept of fractional separation includes a factor for fractional yield and a factor for fractional purity; actual yield and purity can be estimated from the composition of the original mixture, as known or approximated from the experimental curves.

A comparison of the results of fractionation of a specific mixture with an arbitrary volume ratio of 1, and with a volume ratio adjusted according to Equation 8, is given by the calculated curves of Figure 7.

The mixture of 1000 mg. of A ($K_a = 1.0$) and 100 mg. of B ($K_b = 9.0$) is separated far more sharply with the adjusted volume ratio ($V_x/V_y = 0.333$). For this ratio the summation curve shows two distinct peaks, in spite of the small amount of substance B taken at the start, and the X-pool (sum of all the X fractions) contains 96.5 mg. of B and only 35.0 mg. of A. For volume ratio 1 the summation curve does not show two peaks, and the first three X-fractions contain 95.9 mg. of B and the relatively large amount of 144.4 mg. of A. The relative positions of the two peaks of the summation curve with respect to the abscissa will vary little with the initial relative amounts of A and B, but the relative heights of the two peaks will vary directly with these amounts. The peak due to B, for example, will be lower as the amount of this component is less, and may not be obvious if this amount is small while the fractional separation of the components of the mixture is low. For example, a 100% separation of such a mixture would always show the two peaks; on the other hand, if the fractional separation of the mixture is 0.965, as in the example given above, then the minimum of some 5 to 10% of (in this case) component B must have been present originally to produce the second peak. Less than this amount gives a curve which deviates from the "theoretical curve" (for component A in this case) (cf. 8) but gives no graphical indication of the value of p_b.

It seemed very desirable to develop as a practical tool a general relationship between n and the fractional separation of various pairs of substances.

In Figure 8 are plotted data showing the calculated fractional accumulation of single solutes in the X-pool for various values of p and of n. The actual number of extractions represented is always n^2.

For a mixture of substances A and B the fractional separation for any value of n can be read directly from the curves if V_x/V_y is adjusted according to Equation 8 so that $p_a = q_b$. For example, if $p_a = 0.45$ and $p_b = 0.55$ ($K_b/K_a = 1.5$) and $n = 6$, the X-pool will contain 36% of the A and 64% of the B; the Y-pool will contain 64% of the A and 36% of the B (64% separation). The separation of the two substances at $n = 10$ is 67%. By extrapolation of these curves it is indicated that to attain about 85% separation of this mixture some 100×100 extractions would be required. If $p_a \neq q_b$ the curves can still be used to estimate the
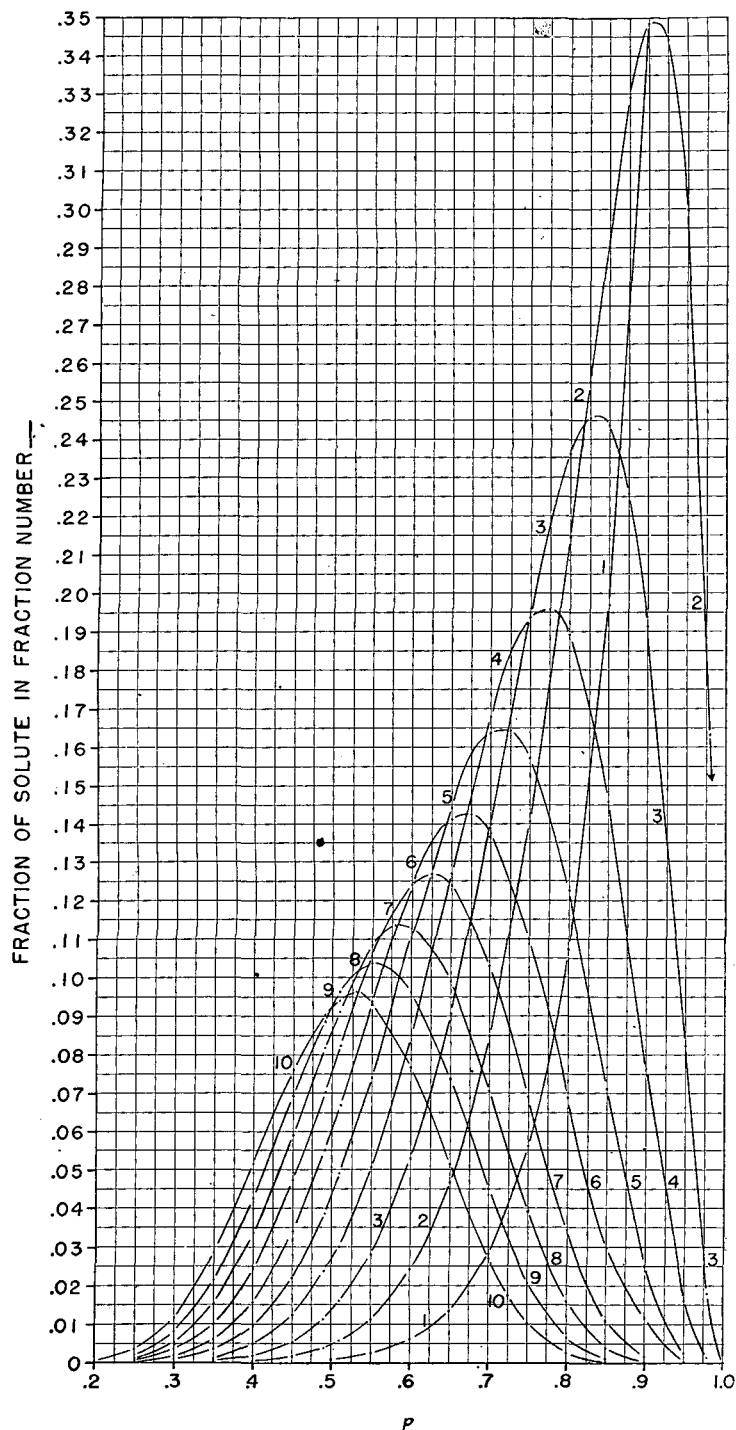

Figure 4. Fractions of Solute in Twenty Fractions for $n = 10$ and All Values of p

Numerical data from a table analogous to Table I. To find values "fraction of solute" in fractions 11, 12, 13, etc., for a given p, find $1 - p$ on abscissa and opposite this find the sought values on curves 10, 9, 8, etc.

fractional amounts of solutes in the X-pool, or in the Y-pool, if the extractions are carried out in the manner shown in Figure 1. Thus, for $p_a = 0.2$ and $p_b = 0.3$ the fractional amounts of the two substances in the X-pool for $n = 4$ will be 0.03 and 0.125, respectively.

It is possible to read from these curves, or estimate between them, the simultaneous fractional accumulations of any number of solutes for which the values of p are known. The use of V_x/V_y as indicated by Equation 8 to attain the maximum degree of separation of any two substances of a mixture will, of course, determine the distributions of all other components of the mixture. Further applications of Equation 8 to further separations can subsequently be made to various other pairs of the component solutes as it becomes possible to estimate other p's.

In Figure 9 fractional separation is plotted against $p_a - p_b$; the values are taken from Figure 8 for $n = 6$ and $n = 10$. The smooth curves represent symmetrical separations. Also shown are points calculated from various area ratios (from Figure 5 and the like).

The use of V_x/V_y other than as calculated by Equation 8 can sometimes be advantageous. It may be desirable to isolate even in small yield one component of a mixture in a state of near-purity. By adjusting V_x/V_y to give a near maximum value to p_a/p_b this goal can often be attained with relatively few extractions. If it is desired to fix p_a at a certain value, the necessary volume ratio can conveniently be calculated from the relationship

$$V_x/V_y = \frac{p_a}{K_a - K_a p_a} \tag{9}$$

which is readily derived from Equation 5. If the Equations 5 for p_a and p_b are put through the operation p_a/p_b, the result can be simplified to

$$\frac{p_a}{p_b} = \frac{1 + \left(\frac{1}{K_b}\right)\left(\frac{V_y}{V_x}\right)}{1 + \left(\frac{1}{K_a}\right)\left(\frac{V_y}{V_x}\right)} \tag{10}$$

From this relationship it can be seen that as V_y/V_x is made larger p_a/p_b gets larger (for $1/K_a < 1/K_b$) approaching K_a/K_b. Large values of V_y/V_x tend to give small values to p_a and to p_b and the curves of distribution tend to be extremely skewed. As n is increased the amounts of both solutes in the X-pool decrease. There is no advantage in carrying this process to the stage where the amount of material present in this pool is reduced below a practical minimum; an unsymmetrical arrangement of the extractions, however, may be advantageously carried through a larger number of extractions. (In this sense "unsymmetrical" and "symmetrical" do not refer to the manner in which the solutes separate, but to the unequal or equal numbers of batches of the two solvents.) A symmetrical arrangement for $p_a = 0.2$ and $p_b = 0.1$ ($K_a/K_b = 2.25$) and $n = 6$ (see Table I) results in the accumulation of 1.17% of the A and 0.03% of the B in the X-pool. An unsymmetrical arrangement would involve holding the number of batches of solvent Y constant at, say, 6 while carrying through a relatively large number of batches of solvent X, say 12 or more. In this way the yield of A in the X-pool is increased, but with gradual diminution of enrichment with respect to A. (Figure 2 can be used to calculate distributions for unsymmetrical arrangements of the extractions, but Table I and Figures 3 and 4 cannot be so used, except for such parts of the unsymmetrical as may be identical algebraically with the symmetrical arrangement.)

There is an analogy between the unsymmetrical procedure and that sometimes used in partition chromatography, where the
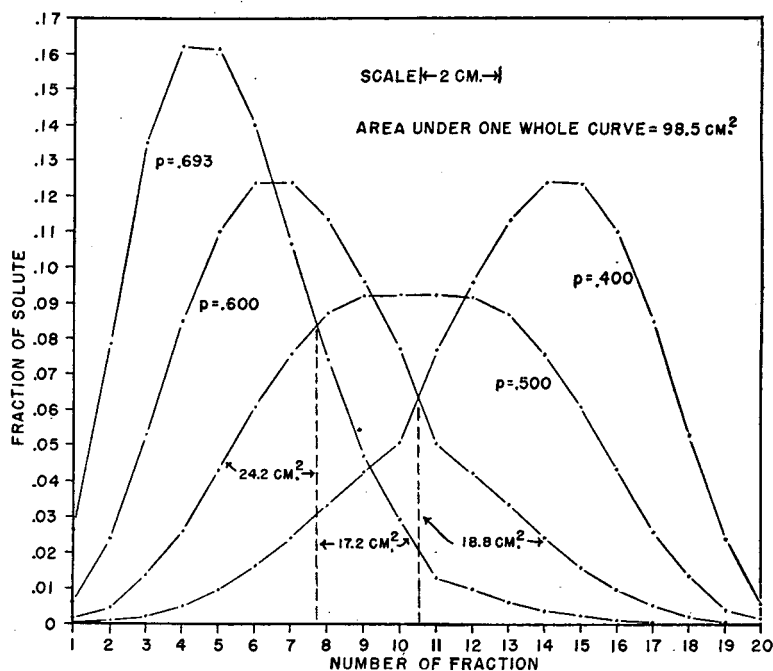
Figure 5. Typical Distribution Curves

Data for points on these curves are taken from Figure 4. Number of extractions represented is $10 \times 10 = 100$. Pairs of curves $p_a = 0.6$, $p_b = 0.4$, and $p_a = 0.693$, $p_b = 0.5$ represent distributions of substances A and B ($K_a = 2.25$, $K_b = 1.00$) when $V_x/V_y = 0.667$ and $V_x/V_y = 1$, respectively
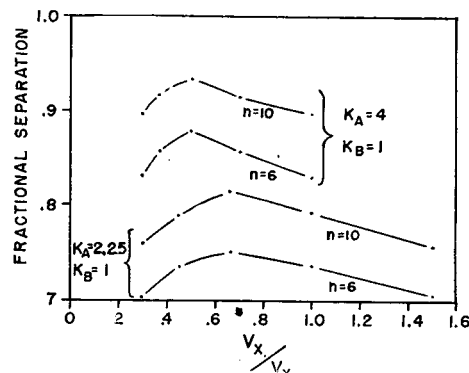
Figure 6. Effects of Variation of Volume Ratio on Fractional Separation of Two Pairs of Substances

Maximum fractional separations occur at values of V_x/V_y given by Equation 8. Ordinate values were calculated from appropriate areas, which were measured with a planimeter on graphs of Figure 5 and the like

volume of the fixed solvent (X) is relatively small and the values of the several K's are made large—for example, by adjusting the pH of solvent X, the aqueous phase—so that the solutes move very slowly through the column (19).

APPLICATIONS OF MULTIPLE FRACTIONAL EXTRACTION TECHNIQUE

The application of fractional extraction methods to various specific separation problems has been studied in great detail by many investigators. Cornish et al. have studied countercurrent extraction as applied to the separation of mixtures of oil-soluble vitamins. Martin and Synge have used the method to separate mixtures of amino acids. Craig has applied the method in a more general way. In this laboratory modifications of the method have been applied to (1) the examination of unknown mixtures, (2) the search for known substances in unknown mix-
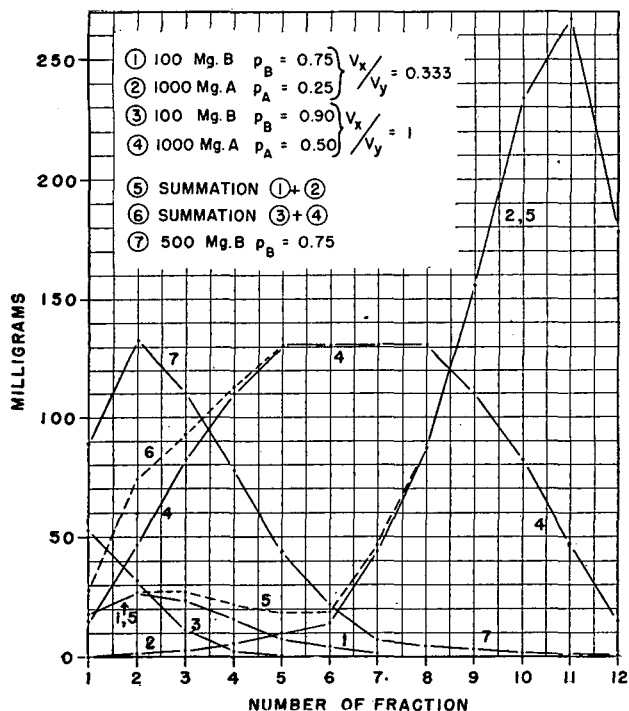
Figure 7.   Separation of Substances *A* and *B*
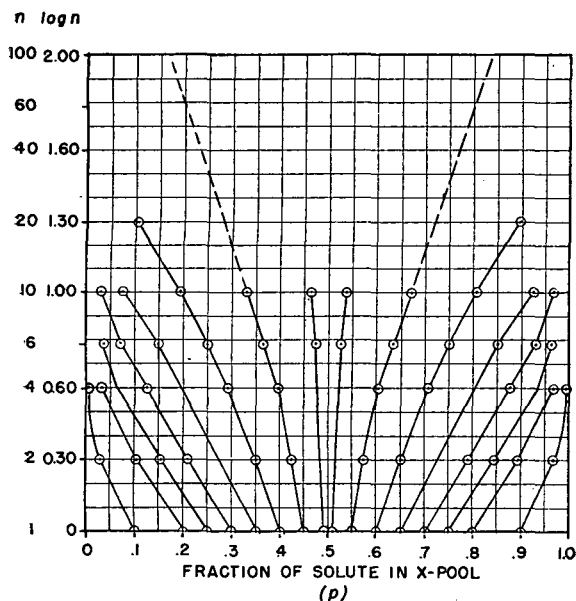
Figure 8.   Fraction of Solute in the *X*-Pool

Values for points indicated are taken from Table I and
the like.   For $n = 1$ curves intersect abscissa at corre-
sponding values of p

tures, (3) the analytical separation of qualitatively known mix-
tures, and (4) the testing of a substance for "purity."   These
applications are briefly discussed below.

1. **Examination of Unknown Mixtures.**   When previous
knowledge of the sought component(s) is not available, the mix-
ture is best subjected to a fractionation procedure essentially
like but not necessarily identical with that used by Craig (*8*).
Adjustment of conditions (pH, volume ratio, and composition
of solvents, etc.) by means of preliminary studies to give initial
p (average for all components) between about 0.2 and 0.8 fol-
lowed by, say, 2 × 2 or 4 × 4 or more extractions will usually
give a considerable amount of information about the compo-

nents of the mixture.   Subsequent fractionations may be based
on volume ratios which will give more efficient separations.
A value of *p* can, of course, be calculated from the experimental
weights or related data for any two adjacent fractions on a di-
agonal without reference to the original quantity of solute or
from either of the two end fractions alone with reference to the
original quantity of solute.   Reference to Figure 8 will give the
approximate value of *n* required to give the desired degree of
separation for any two values of *p*.

For example, derive K_a from the data for fractions 11 and 10
(Figure 7, curve 5)

$$\frac{6pq^6}{21p^2q^6} = \frac{262 \text{ mg.}}{232 \text{ mg.}}, p = 0.25, K = \frac{pV_y}{qV_x} = \frac{3 \times 0.25}{0.75} = 1.0$$

To derive K_b from fractions 1 and 2 (curve 5):

$$\frac{p^6}{6p^6q} = \frac{18.0 \text{ mg.}}{27.8 \text{ mg.}}, q = 0.257, K = 8.6. \text{ (This value of } K_b \text{ differs}$$
from 9.0 because these weights include small amounts of *A*.)

The method has been applied in this general way to the isola-
tion of antibiotics and other substances from cultures of *Asper-
gillus flavus* (*3*, *4*).

2. **Known Substance in Unknown Mixture.**   The search for a
known substance in an unknown mixture can be carried out by
adjusting conditions to give a reasonable value of *p* (0.2 to 0.8)
for this substance and performing an arbitrary number of ex-
tractions—say 4 × 4.   Comparison of the actual amount of total
solute in each fraction with the theoretical fractional amount for
the known substance will give for each fraction a theoretical
upper limit to the amount of this substance which could have
been present in the original mixture.   For example, if a fraction
contains 10 mg. of total solute, and should theoretically contain
10% of the total amount of the known substance present in the
original mixture, then the amount of this substance which could

have been present originally is $\leqq \dfrac{10}{0.10}$ mg. $\leqq 100$ mg.   If it is

desired to set this upper limit lower and/or to isolate the sub-
stance, further extractions will usually be necessary.   Failure to
detect the substance makes it desirable to test the capability of
the procedure to isolate the substance when it is actually added
to the other components—i.e., to test the validity of the basic
assumptions with respect to this particular substance under the
conditions of the experiment.

Figure 9.   Relationship between $p_a - p_b$ (for
$K_a > K_b$) and Fractional Separation

Value of $p_a - p_b$ is a maximum when V_x/V_y is adjusted
according to Equation 8

This use of the method has been made in work on the metabolic fate of narconumal (5), of evipal (2), and of thiobarbital (1).

3. Analytical Separation of Qualitatively Known Mixtures. This can be carried out in the same general manner, except that it is now postulated that the actual values of several K's are known.

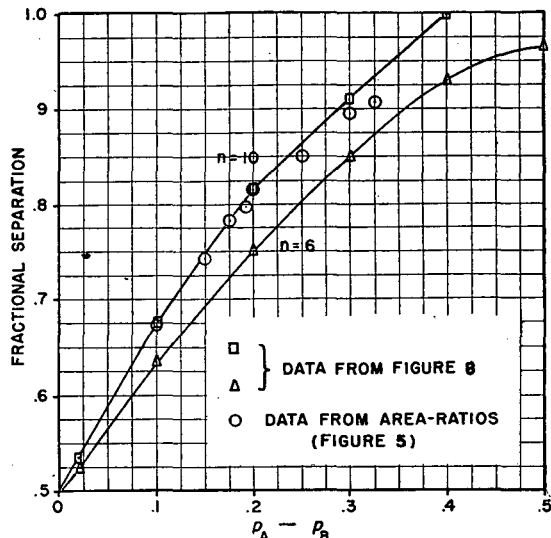For a specific example a mixture of sterols and the data of Cornish et al. (6, Table II) might be discussed. A study of this table shows that for most of the pairs of solvents given, the distribution coefficients of the three sterols, ergosterol (E), cholesterol (C), and sitosterol (S), are very close together. However, the pair of solvents n-C_7H_{16}–CH_3CN give $K_E = 4.4$, $K_C = K_S = 10.2$ (at $0°$ C.); further, the solvent pair iso-C_3H_{18}–C_2H_4ClOH give $K_E = 0.21$, $K_C = 0.36$ and $K_S = 0.65$ (at $-18.5°$ C.). With the first pair of solvents ergosterol can theoretically be separated from cholesterol plus sitosterol as follows: Calculate from Equation 8

$$V(n\text{-}C_7H_{16})/V(CH_3CN) = \sqrt{\frac{1}{4.4 \times 10.2}} = 0.149$$

From Equation 5 $p_E = 0.396$, $p_C = 0.604 = p_S$

Reference to Figure 8 shows the relation between n and the degree of separation theoretically attainable—for example, at $n = 20$ a 90% separation is indicated. The separation of C and S (90% of which are in the n-C_7H_{16}-pool) can now be undertaken with the solvents iso-C_8H_{18}–C_2H_4ClOH; for volume ratio 2.07, $p_C = 0.43$, $p_S = 0.57$ ($p_E = 0.30$) and the separation will be somewhat more laborious than the preceding one. Figure 8 indicates, however, that the separation is by no means impractical, particularly if very high yields are not required—that is, if reprocessing of enriched fractions is used to get high purity at the expense of yield.

In practice it may be advantageous to combine fractional extraction separations with crystallization procedures, since the latter are in general more effective in final purification. For this reason and because of the great labor of carrying out large numbers of extractions the authors have generally used the extraction method to attain no more than about 80 to 90% separation. From data such as those shown in Figure 8 it is clear that whereas a 75% separation can be achieved with only 6×6 extractions ($p_a = 0.6$ and $p_b = 0.4$), 10×10 extractions will be required to separate the same mixture to 81%; and if the goal is set at 90%, 20×20 extractions will be necessary. On the other hand, by reprocessing an X-pool and/or a Y-pool lower yields of higher purity can be obtained.

In the example just given the X-pool after 36 extractions contains 75% of the A and 25% of the B (75% separation). If the solvent X is distilled off until the original volume is reached and this solution is put through 6×6 extractions as before, the new "X_2-pool" will contain $(0.75)^2$ of the A and $(0.25)^2$ of the B—that is, 56 and 6.2%, respectively, of the original amounts. The new "Y_2-pool" will have the same composition as the original mixture. In the same way reprocessing of the first Y-pool will give 56% of the B mixed with 6.2% of the A in a new Y-pool, and the corresponding new X-pool will have the same composition as the original mixture.

4. Testing for Purity. The testing of a substance for homogeneity can be carried to any desired goal, using a procedure similar to (1) above. If the initial p be adjusted between about 0.2 and 0.8 ($p = 0.5$ will give the same amounts of a pure material in the two end fractions, which may be desirable) and n^2 extractions performed, a comparison of the amounts, and properties, of the material in the fractions p^n and q^n will be the most sensitive indication of whether change of composition has been brought about. Homogeneity is indicated if the calculations of p and q from p^n and q^n give the values of p and q which were obtained at $n = 1$. If properties of the two fractions which are very sensitive to change of composition, such as melting point, also are tested, relatively small values of n may give satisfactory tests of purity. (If melting point or other test of change of composition can be used, quantitative study of the distribution of mass of solute becomes less important and deviations from the postulates can be risked by using more concentrated

solutions; maintenance of precise V_x/V_y would also be less important.) If these data do indicate change of composition, the intermediate fractions should be examined carefully and it is helpful to compare the whole distribution curve with a "theoretical" curve derived from a p calculated from a pair of fractions near a maximum in the experimental curve. Further extractions can be based on these results. If one is lucky enough to find two maxima in the experimental curve (see Figure 7) further extractions can be based on the values of two p's estimated therefrom. If the fractions represented on the experimental curve which lie near a theoretical curve are combined and reprocessed, a relatively pure substance is likely to be obtained.

The "purity" of a substance should, of course, be expressed in terms of whatever tests for homogeneity have been applied—i.e., in terms of the amount of impurity of specific relationship to the substance under test (ratio of K's for example) which might not have been detected.

The sensitivity of fractional extraction tests for purity of a substance can be increased by reprocessing enriched fractions—that is, the upper limit to the amount of an impurity of given K which could be present can be set lower, or a smaller amount if present can be detected, with fewer extractions by these reprocessing procedures than by moderately increasing the value of n used in the first place. Even if a countercurrent-distribution machine is available it is still often advantageous to reprocess enriched fractions, as pointed out by Craig (8). Careful study of Figure 8 should be helpful in deciding how large a value of n to use for the given purpose. It is true, of course, that if the practical difficulties can be overcome, the use of very large values of n is the method of choice for detecting small amounts of closely related impurities. Partition chromatography can conveniently be made to give large values of n (18), but the amounts of material which can be used are small.

DISCUSSION

It has been possible to develop a simple treatment of multiple fractional extraction analysis by making the number of postulates as few as possible, and particularly by considering the procedure as a discontinuous batch process. In their mathematical treatments, Cornish et al. (6), Martin and Synge (18), Stene (21), and Craig (8) have presented equations which describe continuous functions; not only are the mathematical difficulties considerable but additional restrictions are generally found necessary to make it possible to treat the system in a continuous way. For example, the volume ratio 1 has often been employed. Cornish et al. (6) used a flow ratio which was the reciprocal of a single partition coefficient. Jantzen (16) mentions, but does not discuss, adjustment of volume ratio to give $p_a = q_b$. Martin and Synge in one of their experiments adjusted the flow ratio of the two solvents to the geometric mean of two partition constants. But they do not discuss the significance of this adjustment, and do not use it in the other experiments. They refer to a forthcoming paper by Daniels and Martin concerning flow ratios and partition coefficient ratios, but this paper has apparently not yet been published.

Study of Figure 8 shows how laborious it is to achieve high degrees of separation when the ratio of the two partition constants is small (<2). It would thus be wise to search diligently for conditions which increase this ratio before trying to separate two closely related substances. For example, among many pairs of solvents one pair may give comparatively advantageous differences between K's [data of Cornish et al. (6), Synge (22), and Craig et al. (12)]. Another approach which is often useful in separating mixtures of acids or bases has been studied recently by Craig and his co-workers (10), and involves the use of aqueous solutions buffered at suitable pH to take advantage of whatever differences in ionization constants exist between the acids or bases.

To illustrate this a separation of formic acid and acetic acid can be considered; partition constants ether/water, respectively, K_f 0.40 and K_a 0.48 (concentration in the aqueous phase approximately 0.02 N) (20). The ionization exponents are, however, $pK_f = 3.67$ and $pK_a = 4.74$. If the aqueous phase is buffered at pH 4.74—for example, with $2 M$ phosphate containing equal amounts of sodium and potassium—the effective partition constants K_f' and K_a' are:

$$K_f' = \frac{K_f}{C_{sf} + C_f} = \frac{0.40}{11.5 + 1} = 0.032$$

and

$$K_a' = \frac{K_a}{C_{sa} + C_a} = \frac{0.48}{1 + 1} = 0.24$$

where C_f and C_a are the concentrations in the aqueous phase of the respective acids, and C_{sf} and C_{sa} are the concentrations of the two corresponding salts. (The acids of the buffer and all salts are assumed insoluble in the nonaqueous phase and to have no effects other than the maintenance of constant pH. In practice, of course, K_f' and K_a' should be approximated experimentally before carrying out the separation.) Thus $K_a'/K_f' = 7.5$ as compared with $K_a/K_f = 1.2$. A 90% separation of the two acids should require only about 4×4 extractions ($V_{ether}/V_{buffer} = 11.4$), although the change of partition constants with dilution (15) and the high concentration of salts in the aqueous phase will cause the distributions to be different from those calculated from the values chosen above. The degrees of ionization of the acids, however, should remain constant at the constant pH of the buffer solution and the partition constants may therefore vary less than indicated in (15).

The choice of pH $=$ pK_a in the example above is arbitrary; it gives much greater K_a'/K_f' than pH $= pK_f$. With some pairs of acids it may be possible to set up the separation described by Equation 8—that is, $K_a' = \dfrac{1}{K_b}$—by proper adjustment of pH alone, but on the basis of the assumptions, it is a minimum prerequisite that at least one of the partition coefficients of the free acids be greater than 1. The separation of bases can be treated in an analogous manner.

Closely related studies of the distribution of mixtures of organic bases between aqueous mineral acids and organic solvents were made many years ago by Jantzen (16) and his students (23).

There is need for improved apparatus to carry out large numbers of extractions on a laboratory preparative scale. The use of such complicated apparatus as that of Cornish et al. or of Martin and Synge is hardly possible in the ordinary laboratory. The machine of Craig is excellent from an analytical point of view, because it makes mechanically feasible the performance of a large number of extractions. The "efficiency" of the method without adjustment of V_x/V_y is, however, appreciably less than that with adjustment according to Equation 8 whenever the two known partition coefficients in question differ from each other in such a way that $K_a \neq 1/K_b$. The advantage of adjustment of the volume ratio in conjunction with carrying the extractions through the diagonal stages is great enough so that for $K_a = 1$, $K_b = 0.5$ the "separation" calculated for one revolution of a 19-plate machine (volume ratio 1, approximately 190 extractions) (see 8, page 531) is almost equaled for substance B and is slightly exceeded for substance A by 10×10 extractions in separatory funnels (volume ratio 1.41). Calculated from the data in Craig's text, $S = 0.769$; for the "diamond" separation, $S = 0.763$.

The new countercurrent distribution machines are made with interchangeable sections which allow the variation of the volume ratio over a reasonable range; a machine of larger capacity will soon be available (9).

In the use of these machines, Craig and his co-workers have recently improved the separations attainable with the fixed number of tubes by using an "alternate withdrawal" technique $(12$, page 677). An adaptation of the machine to the "diamond" arrangement (Figures 1 and 2) can be made after one revolution is completed, by withdrawal of the two end fractions, corresponding to p^n and q^n (in a 25-tube machine, pipet out the upper

layer in upper tube 0 after equilibration with lower tube 24, then turn empty upper tube 0 over lower tube 0 and pipet out lower layer 0) and continuing on a second revolution and withdrawing the two "end" fractions after each equilibration, until the machine is empty.

In most laboratories the separatory funnel is likely to remain the principal apparatus for carrying out extractions. The handling of ten separatory funnels is actually a relatively simple matter (10), and by use of optimum volume ratios and by carrying the process to a stage corresponding to the bottom diagonals of Figure 1 excellent separations can often be achieved. Many separations in the organic laboratory can probably be accomplished satisfactorily with six separatory funnels (or fewer), particularly if fractional crystallization or reprocessing by extraction can also be applied (to enriched fractions). It is for this reason and because of the labor of calculation that the calculated data are presented in terms of the small values of $n = 6$ and $n = 10$.

It may be useful to suggest that the algebraic treatment, applied here to systematic fractionation with two liquid phases, should also be applicable to the analogous fractionation by distribution between one liquid and one solid phase ("systematic multiple fractional adsorption") recently studied by Craig and co-workers (11). The necessary assumption that the "active surface" of the solid phase never be saturated with "solute" would be analogous to the assumption that no excess solute be present in the liquid–liquid systems. It would also be assumed that the active surface of the solid phase is uniform.

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Aromatics in Petroleum Fractions

Separation and Determination from High Boiling Petroleum Fractions by Adsorption

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This paper describes a method for the determination of per cent aromatics with an accuracy of 1% in hydrocarbon mixtures boiling above 200° C. (400° F.). The sample is separated by silica gel into aromatic and nonaromatic fractions which may be used for further analysis. This method classifies all hydrocarbons containing one or more aromatic rings as aromatics whether the side chain is paraffin, olefin, naphthene ring, or cyclo-olefin.

PETROLEUM fractions contain a great variety of hydrocarbons which can be classed as aromatics. Straight-run gasolines contain aromatics which consist of aromatic ring and paraffin chain. In higher boiling straight-run petroleum fractions aromatic hydrocarbons contain aromatic ring, naphthene ring, and paraffin chain as demonstrated by Mair et al. (12, 14). Aromatic hydrocarbons in cracked petroleum samples are even more complicated because olefin double bonds may be present in the rings or chains attached to the aromatic nuclei. Aromatic olefins are not usually found in gasoline fractions since only a few boil within this range—e.g., styrene and indene—but they may be present in considerable quantity in the gas oil and lube oil fractions. Aromatic olefins may cause confusion in hydrocarbon analysis because some analytical methods classify them as olefins, while others classify them as aromatics.

Several methods have been presented in the past few years for determination of aromatics in the gasoline range. Using specific dispersion and bromine number Grosse and Wackher (4) and Groennings (3) have developed a method for aromatic determination which is unsatisfactory when aromatic olefins are present. Kurtz, Mills, Martin, Harvey, and Lipkin (7) have described two methods, one using acid treat and bromine number and the other using acid treat and nitrogen peroxide treat, both of which classify aromatic olefins as olefins. Mair and Forziati (9, 10) have developed two procedures using silica gel for determination of aromatics in low-olefin gasolines. Some of these methods may be extended for use in the kerosene range, but none is satisfactory for higher boiling petroleum fractions such as lubricating oils.

Silica gel has found wide application in the separation of aromatics from petroleum fractions and a great deal of exploratory work has been done by A.P.I. Project 6 at the National Bureau of Standards. Mair and White (13) have studied the separation of binary mixtures in the gasoline boiling range and Willingham (16) has worked on the separation of binary mixtures of high molecular weight.

Silica gel was then put to use for determining per cent aromatics in gasolines. Mair and Forziati (10) developed a method based on volume of aromatic-free percolate, but this required calibration with mixtures similar in composition to the unknown mixture. Mair then developed a simpler method (9) based upon a plot of refractive index versus volume of percolate which is satisfactory for low-olefin gasolines.

The next development by Mair and Forziati (11) was the application of silica gel to the complete separation of aromatics from mixture with paraffins and naphthenes. This is accomplished by percolating the sample through a calculated quantity of silica gel (varies with aromatic content) and washing with large quantities of pentane to remove the paraffins and naphthenes. The aromatics are then displaced from the gel by a suitable desorbent such as methyl alcohol. Very little of the work done by A.P.I. Project 6 has been concerned with hydrocarbon mixtures containing olefins.

In the present work the Mair and Forziati (11) procedure with several modifications has been adapted to the determination of aromatics in all higher boiling petroleum fractions, either straight-run or cracked. The advantages of this method are that it is a standard procedure which can be used without advance knowledge of the aromatic or olefin content of the sample and that it is satisfactory for the more viscous petroleum fractions.

The present method involves dilution of 100 ml. of sample with an equal volume of pentane, percolation through a fixed quantity of silica gel, washing the gel with pentane until the refractive index of the percolate drops to the refractive index of the pentane, and desorption of the aromatics with benzene and methyl alcohol. With the refractive index of pentane as an indication of cut point, two fractions are collected: the first fraction, washed through with pentane, contains the paraffins, naphthenes, and nonaromatic olefins; and the second fraction, obtained by desorption with benzene and methyl alcohol, contains all the aromatics and aromatic olefins and most of the nonhydrocarbons. Since this procedure is used on fractions boiling above 200° C. (400° F.), it is relatively easy to distill the solvents (pentane, benzene, and methyl alcohol) from the separated fractions using a stripper which has been designed for this work. Quantitative recovery of the separated hydrocarbons is obtained, and the fractions are available for further testing.

APPARATUS

The gel column consists of a glass tube 5 cm. in inside diameter by 120 cm. long with a stopcock at the bottom. The receiver, usually a 1-liter graduate, is immediately underneath the stopcock.

A refractometer capable of giving refractive indices reproducible to 0.0001 or 0.0002 is necessary. A Valentine precision Abbe-type refractometer is used in this laboratory. For most of the work reported here, it was convenient to use a special through-flow refractometer placed in series between the column and receiver to follow the change in composition of the effluent. The connecting lines were made as short as possible to minimize holdup.

The stripping apparatus (Figure 1) consists of a 500-ml. separatory funnel leading to a 250-ml. round-bottomed flask through a short distilling head with side arm attached. The side arm leads down into a 500-ml. flat-bottomed flask. The 250-ml. round-bottomed flask is immersed in a water bath heated by a 1-liter hemispherical Glas-col heater. A piece of tubing drawn to a small opening also comes down through the distilling head to within a short distance of the bottom of the 250-ml. distilling flask. Spherical joints allow the disconnection of the side-arm tubing, the 500-ml. separatory funnel, and the 250-ml. round-bottomed flask.

An inexpensive laboratory beam balance is used to weigh the samples with an accuracy of ±0.05 gram. A wire attachment is used, so that the 250-ml. round-bottomed flask may be easily weighed.

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MATERIALS

Silica gel, 28- to 200-mesh, supplied by Davison Chemical Corp. is used. Its adsorptive capacity should be such that on percolation of 20 ml. of a standard mixture, 20% benzene in methylcyclohexane, through 10 grams of gel in a 10-mm. inside diameter column, no less than 5 ml. of aromatic-free filtrate will be obtained as determined from the refractive indices of small portions of the filtrate.

Solvents used are pentane (any mixture of pentanes boiling between 30° and 40° C.); benzene; and methyl alcohol. The solvents should be free from high boiling residue, since this would make it difficult or impossible to separate the solvent completely from the concentrate by distillation.

PROCEDURE

1. Approximately 100 ±1 ml. of sample are weighed out with an accuracy of ±0.05 gram and diluted with 100 ml. of pentane.

2. A small wad of glass wool is tamped into the bottom of the glass column. One kilogram of silica gel is weighed out and introduced into the glass column, being tamped as it is charged in order to minimize channeling.

3. Five-hundred milliliters of pentane are introduced into the column and the bottom stopcock is opened.

4. When the pentane just disappears into the gel, the diluted sample is added, with care that none of the oil sample is lost (the sample container is rinsed with small portions of pentane).

5. As the liquid level falls to the level of the gel, two 500-ml. portions of pentane and then as many 200-ml. portions of pentane as necessary (see paragraph 7) are added successively to the column to displace the nonaromatic hydrocarbon fraction from the gel, and the percolate is collected in a graduated receiver. The flow is regulated at 7 ± 1 ml. per minute.

6. Approximately 1-ml. samples of the percolate are collected at specified intervals for the measurement of refractive index, and any sample left after measurement is returned to the graduated receiver. Refractive index measurements are made after 100 and 1000 ml. of percolate are collected and at 100-ml. intervals thereafter until the refractive index is within 0.0002 of the first refractive index measured—that is, the refractive index of the pentane itself, which was measured after the first 100 ml of percolate were collected.

7. When the refractive index of percolate is within 0.0002 of refractive index of pentane, no more pentane is added to the top of the column. At this point the desorption of aromatics is started with a mixture of 400 ml. of benzene plus 100 ml. of methyl alcohol. Two 500-ml. portions of methanol are later added to the column to complete the desorption.

8. Two interfaces appear as the desorption proceeds down the column, the lower interface indicating the position of the ben-

Figure 1. Distillation Apparatus

zene front and the more pronounced upper interface showing the position of the methanol. When the lower interface is three fourths of the way down the column, the receiver is changed and collection of the aromatic fraction is begun. The volume of the first fraction is usually between 1600 and 2000 ml.

9. The rate of flow of percolate may decrease during collection of the second fraction, even though the stopcock is fully opened. While the column is draining, the stripping apparatus (Figure 1) is made ready for use and tare weight is obtained on the 250-ml. round-bottomed flask.

10. The two fractions are separately stripped of the solvents, pentane, benzene, and methanol, and 500 ml. of the fraction are poured into the separatory funnel and allowed to drain into the 250-ml. round-bottomed flask until the latter is half filled. Then the stopcock on the separatory funnel is closed. The water bath is gradually heated and a small stream of nitrogen is admitted through the capillary to prevent bumping. When the solvent begins to distill, the stopcock on the separatory funnel is opened and the sample let into the flask at a rate approximately equal to solvent take-off. (The second fraction of percolate may contain some "fines" from the silica gel, in which case this percolate must be filtered into the separatory funnel and the filter washed with pentane.)

11. If the original sample has an initial boiling point near 200° C. (400° F.) the temperature of the water bath is kept below 85° C. to minimize losses. With lube oil samples, the water bath temperature is kept above 95° C.

12. As the separatory funnel empties, it is refilled with sample until the sample is exhausted. All the remaining sample is washed into the flask by a few rinses with pentane.

13. The solvent is collected in the cooled receiver until drops of solvent stop forming at the end of the delivery tube leading into the receiver. At this point the flask containing the stripped sample is disconnected from the separatory funnel and the receiver, and the flask is heated in the water bath for an extra hour.

14. The flask is then weighed, heated one hour more, and reweighed. The operation is repeated until agreement within 0.1 gram is obtained.

15. The weight of the nonaromatic hydrocarbon fraction plus the aromatic fraction must equal at least 98% of the sample charged, or the analysis is repeated.

16. The density of each fraction is taken and the volume % aromatics calculated from the equation:

$$\text{Volume \% aromatics} = \frac{\dfrac{\text{weight of aromatics}}{\text{density of aromatics}}}{\dfrac{\text{weight of aromatic}}{\text{density of aromatic}} + \dfrac{\text{weight of nonaromatic}}{\text{density of nonaromatic}}} \times 100$$

Thus the small loss is apportioned between the two fractions.

Discussion. With highly olefinic samples, it may be necessary to use more than 2000 ml. of pentane to cause the refractive index of the percolate to reach the proper minimum.

With very unusual samples the capacity of the gel may be exceeded and the refractive index of the percolate may begin to rise without dropping to the refractive index of the pentane. In this case the minimum refractive index reached should be used for the cut point and the receiver changed to collect the aromatic fraction. If the refractive index of the pentane is not obtained, the capacity of the gel may have been exceeded, and a check determination should be made using 80 ml. of sample instead of 100 ml. If the results obtained using 80 ml. of sample differ from the first determination, the second determination is the correct result.

If the first fraction of percolate shows a brownish coloration, it is desirable to rerun the sample on a different batch of gel. This coloration results from an excessive amount of impurity on the silica gel. The gel obtained from the manufacturer usually contains only a trace of brownish impurity which has no appreciable effect on the accuracy of the method or on the properties of the recovered fractions.

Several investigators have studied the use of different desorbents for aromatic hydrocarbons. Gooding and Hopkins (2) state that for fractions boiling below 325° C. "the three most useful desorbents so far tested are isopropyl alcohol, Carbitol, and 2-methyl-2,4-pentanediol." When these desorbents are used, they are separated from the oil by water washing. The authors' experience has been that separation of the desorbent by distilla-
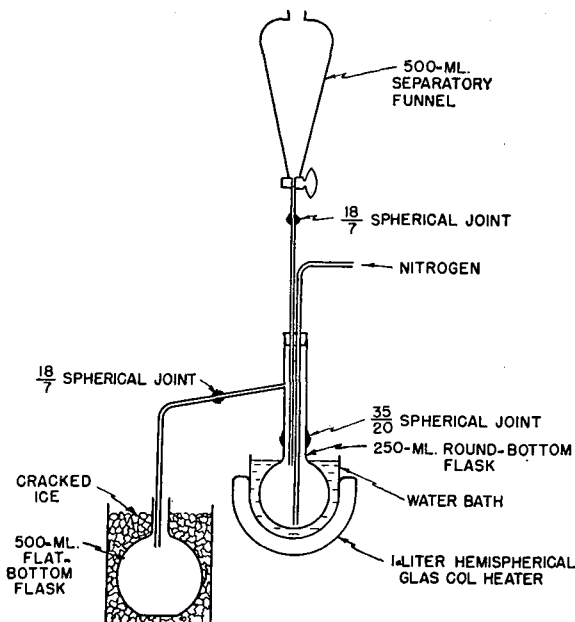
Table I. Accuracy for Known Blends in Gas Oil Range

(Boiling range 230° to 340° C., 450° to 640° F.)

Physical Properties of Fractions Used in Blends

Aromatics	Saturates
$d_4^{20} = 0.9590$	$d_4^{20} = 0.8674$
$n_D^{20} = 1.5409$	$n_D^{20} = 1.4702$
$\delta = 171 \times 10^{-4}$	$\delta = 96 \times 10^{-4}$
Br No. $= 9$	Br No. $= 1$

Volume % Aromatics Blended	Deviation of Exptl. Volume % Aromatics	Deviation of Experimental Values 10⁴					
		Aromatics			Saturates		
		Δd_4^{20}	Δn_D^{20}	$\Delta \delta$	Δd_4^{20}	Δn_D^{20}	$\Delta \delta$
0.0	0.0	..	..	..	− 6	+ 4	0
5.0	0.2	+ 5	−14	−2	−10	+ 3	0
24.9	−0.1	+ 1	+ 9	0	+ 3	+ 3	0
49.9	−0.4	+24	+10	0	+ 6	+ 2	0
74.9	−0.8	+ 4	+14	+1	− 7	+ 6	+1
95.0ᵃ	−0.5	− 7	+ 8	+1	+20	+17	+2
100.0ᵃ	−0.6	+14	+14	+1	..	..	...

ᵃ 80-ml. sample analyzed.

tion rather than by water washing yields better recovery of the oil. Although methyl alcohol is a good desorbent which can be easily separated by distillation from the aromatics in the gas oil and lube oil ranges, it is not completely miscible with these aromatics. However, a combination of benzene and methyl alcohol makes a satisfactory desorbent for these boiling ranges.

DISCUSSION OF DATA

The method has been tested on synthetic blends of aromatic and saturated hydrocarbons separated from natural petroleum samples in the gas oil and lubricating oil boiling ranges. [Gas oil refers to the boiling range intermediate between gasoline and lubricating oil fractions, approximately 200° to 350° C. (400° to 700° F.)] These tests have shown that the accuracy is independent of aromatic concentration and of boiling range.

Table I shows the analysis of a series of blends of aromatics and saturates separated by silica gel from a petroleum fraction boiling from 230° to 340° C. (450° to 640° F.). Physical properties of the aromatic and saturate concentrates are shown in Table I. The aromatic concentrate contains no more than 1% saturates by an independent analytical method (unpublished). This is comparable to the 0.6% saturates found by the silica gel method (last item of Table I). The saturated hydrocarbon fraction contains less than 1% aromatics, judging from the small change in physical properties on repercolation through silica gel (first item of Table I).

Per cent aromatics has been determined with an accuracy better than 1% on the five blends, which range from 5 to 95% aromatic concentration. Total weight recovery was 98 to 99% in every case. In Table I the physical properties of the fractions separated in each analytical run are compared with the physical properties of the original aromatic and the original saturate. The
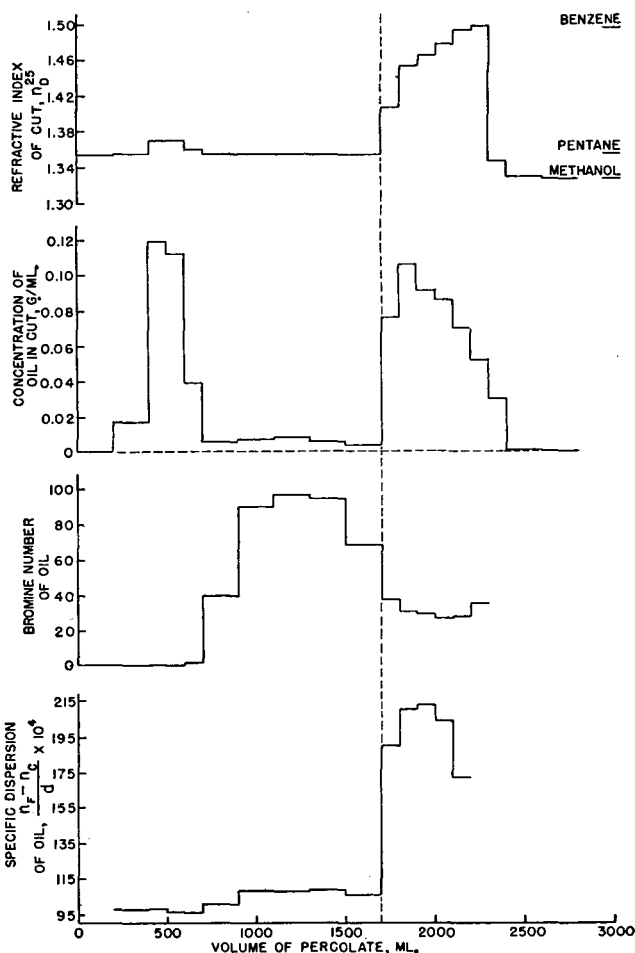
Figure 2. Silica Gel Separation of a Thermal Cracked Gas Oil Boiling at 400° to 620° F.

average deviation of d_4^{20} and n_D^{20} is 0.001. The maximum deviation is 0.002. These properties prove that good analytical separations were made throughout the concentration range.

Table II shows a similar test of blends in the lube oil boiling range. The aromatic fraction and the saturated fraction were separated, using silica gel, from a straight-run lubricating oil boiling from 320° to 450° C. (600° to 850° F.). The saturated fraction contained no aromatic and the aromatic fraction contained 99.7% aromatic when tested with the present method. Blends made at 20, 50, and 80% aromatic concentration were analyzed with an accuracy better than 1%. Physical property measurements on the separated fractions from these analytical runs agree with the properties of the original aromatic and the original saturate within 0.001 on both density and refractive index, except in one case where the deviation was 0.0016. Recovery in each of these determinations was approximately 99%.

The aromatic concentrates from the straight-run gas oil and lube oil, Tables I and II, show significant bromine numbers by the method of Johnson and Clark (6). At present the authors do not know whether these bromine numbers are caused by non-

Table II. Accuracy for Known Blends in Lube Oil Range

(Boiling Range 320° to 450° C., 600° to 850° F.)

Physical Properties of Fractions Used in Blends

Aromatics	Saturates
$d_4^{20} = 0.9974$	$d_4^{20} = 0.8918$
Br No. $= 13$	$n_D^{20} = 1.4851$
	$\delta = 96 \times 10^{-4}$
	Br No. $= 2$

Volume % Aromatics Blended	Deviation of Exptl. Volume % Aromatics	Deviation of Experimental Values				
		Aromatics		Saturates		
		$\Delta d_4^{20} \times 10^4$	ΔBr No.	$\Delta d_4^{20} \times 10^4$	$\Delta n_D^{20} \times 10^4$	ΔBr No.
0.0	0.0	..	...	6	3	0
20.0	0.3	−9	−1	−7	−2	0
50.0	−0.3	10	+1	−2	−3	0
80.0ᵃ	−1.0	16	−1	−1	+4	0
100.0ᵃ	−0.3	1	−1	...	...	..

ᵃ 80-ml. sample analyzed.

Table III. Accuracy for Gas Oil Blends Containing Known Amounts of Nonaromatic Olefin

Physical Properties of Starting Materials

Aromatics	Saturates	n-Octadecene-1
$d_4^{20} = 0.9590$	$d_4^{20} = 0.8674$	$d_4^{20} = 0.7888$
$n_D^{20} = 1.5409$	$n_D^{20} = 1.4702$	$n_D^{20} = 1.4448$
$\delta = 171 \times 10^{-4}$	$\delta = 96 \times 10^{-4}$	$\delta = 106 \times 10^{-4}$
Br No. = 9	Br No. = 1	Br No. = 63

				Deviation of Experimental Values					
			Experi-mental	Aromatics			Nonaromatics[a]		
Blend No.	Volume % Octadecene Blended	Volume % Aromatics Blended	Volume % Aromatics	$\Delta d_4^{20} \times 10^4$	$\Delta n_D^{20} \times 10^4$	ΔBr No.	$\Delta d_4^{20} \times 10^4$	$\Delta n_D^{20} \times 10^4$	ΔBr No.
1	45.0	45.0	45.0	−10	− 5	0	− 3	−2	0
2	45.0	10.0	10.5	−69	−40	3	−14	−2	0
3	10.0	44.9	44.5	+16	+ 7	0	−10	0	0

[a] Properties of saturates plus n-octadecene-1 mixtures calculated assuming volume % additivity of d_4^{20} and n_D^{20}, and weight % additivity of bromine number.

hydrocarbons, bromine-reactive aromatics such as anthracene and its derivatives, or aromatic olefins. The saturated fractions separated from the gas oil and lube oil show bromine numbers of 1 and 2, which may be considered negligible.

When catalytic and thermal cracked petroleum fractions were separated by this method, appreciable bromine numbers were found on both the aromatic and nonaromatic fractions. There-fore a detailed study was made of the separation of the olefins by this silica gel method, using a thermal gas oil of 205° to 330° C. (400° to 620° F.) boiling range which was percolated in the usual manner, except that the effluent was collected in small fractions, each of which was then stripped of solvent. Data on this thermal gas oil are:

Volume % aromatics = 54.8
$d_4^{20} = 0.9014$
$n_D^{20} = 1.5079$
Specific dispersion $\times 10^4$ = 157
Mol. weight = 170 [From density and mid-boiling point by method of Mills, Hirschler, and Kurtz (15).]

Bromine No. = 25.6

Figure 2 shows data obtained on the silica gel percolate. The vertical dotted line indicates the normal cut point for the separation of aromatics from nonaromatics. The upper graph shows the refractive indices of the cuts as collected and the initial increase in refractive index followed by decrease to the refractive index of pentane. The second graph shows the concentration of oil in each cut, and in particular that a 200-ml. cut immediately preceding the cut point contains less than 1% of the original oil. The third graph shows the bromine number of the oil in each fraction. The first few fractions contain no olefin. Bromine number then rises sharply and shows that three or four fractions are almost entirely olefinic. The bromine number drops sharply at the cut point and remains nearly constant through the aromatic fractions. The lower graph shows the specific dispersions of the oil fractions. The low specific dispersions before the cut point show definitely that these olefins are nonaromatic olefins. The high specific dispersions after the cut point indicate that these fractions consist mainly of aromatics.

To prove that this method completely separates the nonaromatic olefins with the paraffins and naphthenes, three blends were made of n-octadecene-1 with aromatics and saturates from the same gas oil used in the blends shown in Table I. Table III shows that volume per cent aromatic was obtained with an accuracy of 0.5% or better on each of these three blends. Densities, refractive indices, and bromine numbers of the recovered fractions are in good agreement with those of the original components except in blend 2 where there is a high ratio of olefin to aromatic, 45% octadecene, and 10% aromatics. In this case the differences in properties of the recovered and original aromatic fractions show that $1/45$ of the octadecene remains with the aromatic. This accounts for an error of 0.5% in the determination

of aromatic content, which is negligible.

It would be interesting to investigate the behavior of other olefin types such as cyclic olefins or diolefins. The data in Table III show that a noncyclic olefin is completely separated from the aromatics, but it is probably a little more difficult to separate cycle olefins. No further work has been done because of the scarcity of pure olefins of high molecular weight. Conjugated diolefins, in particular, may interfere with the sharp separation of nonaromatics from aromatics.

The accuracy of the method is 1% or better on all the blends shown in Tables I, II, and III. Precision of the method is better than 1%, as shown by check determinations on a thermal gas oil which gave 53.8, 55.1, and 55.4% aromatics and check determinations on a lube oil which gave 39.4 and 39.3% aromatics.

APPLICATION TO PETROLEUM SAMPLES

Except for the work of A.P.I. Project 6 on the types of aromatics in a Mid-continent crude (14), there has been practically no work on the types or quantity of aromatics present in the

Table IV. Analyses of Lubricant Fractions from Four Crudes

(Boiling range, 340° to 450° C., 650 to 850° F.)

Crude	East Texas	Michigan	Webster (Harris Co., Texas)	Mirando (Duval Co., Texas)
	Original			
Volume % aromatics	25.7	29.0	29.5	49.3
d_4^{20}	0.8740[a]	0.8664	0.8979	0.9425
n_D^{20}	1.4889[a]	1.4841	1.4955	1.5217
Refractivity intercept	1.0519	1.0509	1.0465	1.0505
Specific dispersion × 10^4	128	126	122	140
Vis100, cs.	15.4	12.7	25.7	56.4
Vis210, cs.	3.31	2.99	4.04	5.37
Viscosity index	89	97	25	−42
Viscosity-gravity constant	0.840	0.834	0.860	0.907
Mol. weight[b]	328	320	326	308
Bromine No.	5.9	6.5	5.1	7.9
	Aromatics			
d_4^{20}	0.9857	0.9575	0.9742	0.9879
n_D^{20}	1.5642	1.5449	1.5478	1.5568
Refractivity intercept	1.0714	1.0661	1.0607	1.0630
Specific dispersion × 10^4	198	181	167	174
Vis100, cs.	68.1	24.8	80.4	127.8
Vis210, cs.	5.59	3.80	5.95	6.69
Viscosity index	−78	−5	−89	−180
Viscosity gravity constant	0.962	0.934	0.945	0.960
Mol. weight[b]	297	304	299	284
Bromine No.	14.9	12.8	12.4	12.9
% sulfur	1.1	2.5	0.7	0.7
	Nonaromatics[c]			
d_4^{20}	0.8345[d]	0.8296[a]	0.8648	0.8971
n_D^{20}	1.4619[d]	1.4595[e]	1.4733	1.4867
Refractivity intercept	1.0447	1.0447	1.0409	1.0381
Specific dispersion × 10^4	99	98	97	96
Vis100, cs.	12.0	10.5	18.8	32.4
Vis210, cs.	3.03	2.76	3.64	4.62
Viscosity index	124	118	75	35
Viscosity gravity constant	0.798	0.795	0.825	0.856
Mol. weight[b]	331	320	331	338
Bromine No.	0.2	2.4	1.2	2.2
% sulfur		All less than 0.1%		

[a] Corrected from 30° C. using temperature coefficient of density of Lipkin and Kurtz (8).
[b] Molecular weights obtained from Vis100 and Vis210 by method of Hirschler (5).
[c] The nonaromatic fractions from East Texas and Michigan contained some wax at 20° C.
[d] Corrected from 37° C. as above.
[e] Corrected from 25° C. as above.

lubricating oil boiling range of petroleum. Table IV shows the aromatic content and properties of the 340° to 450° C. (650 to 850° F.) fractions from East Texas, Michigan, Webster (Harris County, Texas), and Mirando (Duval County, Texas). These crudes contain 26, 29, 30, and 49% aromatics, respectively. On the recovered aromatic fractions molecular weights are nearly the same, but there are considerable variations in the physical properties, expecially in viscosity. East Texas has the lowest aromatic content (even lower than Michigan), but the specific dispersion of the aromatics is higher than in the other crudes. The bromine numbers on the aromatic fractions are in the range 12 to 15, which could indicate as much as 25% aromatic olefins in each sample, but it is more likely that the bromine numbers are caused by nonhydrocarbons or bromine-reactive aromatics. The physical properties of the nonaromatic portions are different, indicating large variations in proportion of ring and chain in the various samples. The bromine numbers are very low, showing that there is little if any nonaromatic olefin in these crudes.

Percentages of sulfur obtained on the aromatic and nonaromatic fractions from these four oils show that essentially all the sulfur compounds have been concentrated in the aromatic fraction. Dineen, Bailey, Smith, and Ball (1) have found that sulfur and nitrogen compounds are not collected in the saturated hydrocarbon fractions but appear in the aromatic fractions. However, they have also shown that some of the more basic nitrogen compounds are so strongly adsorbed that they are not removed from the gel by an alcohol desorbent. If such compounds are present to an appreciable extent in any sample run by the procedure presented in this paper, it may be impossible to obtain the recommended minimum recovery of 98%. Relatively little is known at present about the nonhydrocarbon content of the higher boiling petroleum fractions.

This method has been used successfully on a wide variety of samples including catalytically cracked, thermal cracked, and straight-run petroleum fractions. If the petroleum fraction contains wax which is not dissolved on the first dilution of sample pentane, more pentane can be used or the sample can be percolated at a temperature sufficiently high to keep the wax in solution. If the sample contains considerable asphaltic or tarlike material, these materials can be removed before the percolation by methods such as propane deasphalting or selective adsorption.

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Identification of Small Amounts of Organic Compounds by Distribution Studies

Purity of Synthetic Antimalarials

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IN ORDER to identify an unknown compound by the accepted procedures of organic chemistry, suitable characteristic physical constants such as melting point, boiling point, refractive index, etc., are required. However, before such constants can be reliably used for identification, proof must be obtained that the particular sample used for the determination of the constants is indeed only a single chemical individual.

From almost every standpoint the problem of proving or disproving the purity of a particular preparation of a compound is of fundamental importance for experimental organic chemistry and has been since the very beginning of the science. No single approach to the problem can be applied to every type of compound or individual preparation, but each presents its own difficulties. With most simple organic compounds of relatively low molecular weight which can be distilled or crystallized, a purity sufficient for many purposes can be achieved and demonstrated without too much difficulty. That this type of compound is usually chosen for classroom experiments perhaps accounts for the fact that in textbooks so little space is devoted to the very important subject of purity.

The question of purity is becoming more important to biochemistry, pharmacology, and clinical medicine because a small percentage of a highly active impurity can modify greatly the response expected. Biochemistry is increasingly concerned with more complicated substances of higher molecular weight and, in general, these substances do not show so much shift in properties with minor changes in structure as do the simpler substances. The presence of substantial percentages of isomers or of homologs is therefore frequently not realized. Ultimate analysis and molecular weight determination likewise are not so significant for large molecules in demonstrating the absence of small percentages of homologs. Highly efficient fractional distillation cannot be applied beyond a certain molecular size. All too frequently these substances do not crystallize readily; and more than one substance tends to appear in the same crystal and in nearly the same proportions as was present in the original solu-

The problem of proving or disproving the purity of a given preparation of an organic compound is becoming increasingly important. Classical methods involving determination of melting point, freezing point, boiling point, cooling curves, etc., combined with attempts to fractionate by some procedure are reliable only for compounds completely stable under the conditions of study. Of the many compounds included in organic chemistry, and particularly biochemistry, many, if not the majority, do not possess this stability. Most of the synthetic antimalarials are in this class and a method for demonstrating purity was therefore needed. In this paper the authors report part of their experience in applying the "solubility" method and the "countercurrent distribution" method to the synthetic antimalarials.

tion. Failure of mixtures to give a melting point depression also seems to occur more frequently for more complicated substances.

All these difficulties have recently been encountered in the attempt to synthesize antimalarials of the atabrine or quinoline type such as plasmochin. Here it was highly desirable to furnish the pharmacologist not only with materials in a high state of purity but also to give unequivocal proof and documentation in so far as possible, so that if unexpected toxicity or variation in the biological results appeared, the question of the purity of the sample employed could not be raised.
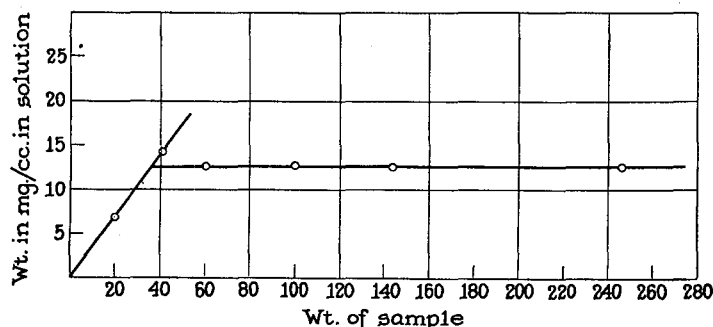
Figure 1. Solubility Curve of Sample 1 of 7618

When this problem was first encountered in the authors' work, the most promising approach appeared to be that of a method which referred to the phase rule. The possibilities along this line have been so well discussed by Northrop and Kunitz (8, 10) and Herriot (6) that they do not require discussion here. From these papers it is clear that the proper use of the "solubility method" is capable of giving data perfectly reliable from both the practical and theoretical standpoint. It has been applied recently to DDT preparations (12). In choosing this method of approach to the problem, the possibilities inherent in the use of cooling curves (11) were considered but the method was not actually tried, since most synthetic antimalarials are furnished as salts which crystallize poorly or are not stable at the melting point.

SOLUBILITY METHOD

A representative example of experience with the solubility method is shown in its application to the drug 7618, 7-chloro-4-(4-diethylamino-1-methylbutylamino)-quinoline diphosphate,

$$CH_3\overset{\overset{\displaystyle H}{|}}{C}-CH_2CH_2CH_2-N\overset{\nearrow C_2H_5}{\searrow C_2H_5}$$
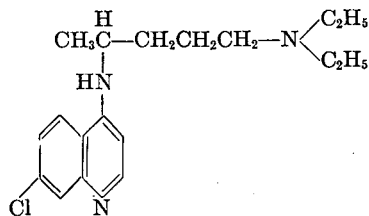
I

Formula I. The number 7618 is that assigned by the Antimalarial Survey. This drug was given to the authors as the diphos-

phate-containing solvent of crystallization (4). The micro hot stage melting point did not appear to be definite but was a decomposition point rather than a true melting point. The melt failed to recrystallize on cooling. Difficulty was also experienced in obtaining the most precise ultimate analysis, except for the phosphorus determination.

In applying the solubility method, that combination of solvents was chosen which appeared to give the most sharply defined crystals in attempts to recrystallize the drug. This seemed a logical choice in order to reduce the time required for equilibration as much as possible. The weight of substance in solution after equilibration was determined by the loss in weight of a sample caused by a standard volume of solvent as described in the procedure of Moore and Stein (9) for the determination of amino acids by the solubility method. The use of weight rather than some other analytical procedure in the determination of the amount in solution is preferable by virtue of the fact that weight is all-inclusive. Equilibrium points were approached from both the supersaturated and nonsaturated state wherever experimentally possible. Figure 1 is a typical result.

Although it should be possible theoretically to use the method for any solvent which dissolves a sufficient amount of the substance, many cases were found where the method was impracticable, presumably because of the erratic rates of crystallization and the persistent tendency to give supersaturated solutions. Another difficulty was that of choosing reproducible drying conditions for the salt after filtration. This latter point was solved by adding a few drops of the solvent to a weighed sample of the salt as received and then drying it to constant weight at the same time and under the identical conditions as the crystals for the determination were dried. The loss in weight of the control so obtained was then used to correct the weights of the filtered crystals. Because of slowness in drying, the entire process required many weighings over a period of several days' time and proved to be a rather tedious procedure. Though this would not be a serious objection for a limited number of preparations, the authors were confronted with large numbers of separate preparations which were mainly of different compounds. Some other method was therefore needed.

In general, aside from the phase rule type of study, proof of purity has been mainly a problem of fractionation. A substance has been considered pure when the most efficient fractionation applicable has failed to cause resolution or shift of either analysis or physical properties. Though this approach is not so all-inclusive as that of the phase rule, it can be applied to many cases unsuitable for the latter and does have the advantage of leading to the isolation of the possible impurity. It is an approach, however, which is also time-consuming and can be abused greatly if the investigator is not sufficiently persistent. Unfortunately, it led to many misinterpretations in the earlier part of the antimalarial search.

COUNTERCURRENT DISTRIBUTION

In previous papers of this series (1, 3, 7) the possibilities inherent in the use of the countercurrent distribution method for

establishing purity have been mentioned. It was therefore considered a promising approach to the present problem as a supplementary and perhaps more rapid method than a solubility study. A considerable number of preparations were therefore investigated by both this method and the solubility method in order to learn if significant differences would be shown. A typical result of a distribution analysis, shown in Figure 2, was obtained on the same preparation used for the solubility curve shown in Figure 1. Approximately 2 molar phosphate buffer at pH 6.54 and chloroform were used as the system. Nineteen transfers were applied at room temperature.
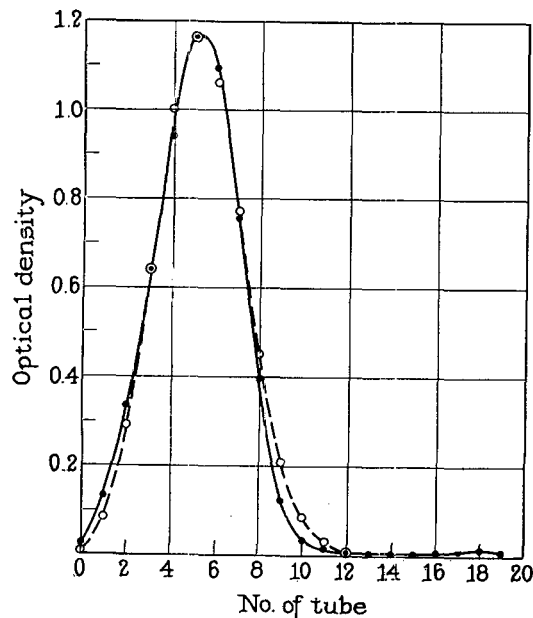

Figure 2.   Countercurrent Distribution Pattern of Sample 1 of 7618

A calculated curve (13) is superimposed. It can be seen that the experimental curve deviates to the left in a consistent way for the lower concentrations and a deviation from a linear partition isotherm is thus indicated (2). That the deviation is indeed due to this was then shown by measuring the partition ratio at several concentrations, but more important from the standpoint of this determination, the partition ratios of the material in tubes 1 and 9 were measured in the same system used for the distribution and found to be identical. The purity of the material occurring in tubes 0 to 10 is thus shown as far as this particular system is concerned.

A small amount of material could be detected spectroscopically in tubes 15 to 19. The partition ratio of this material (concentrations determined spectroscopically) proved to be widely different from that in the main band and it must be regarded as impurity. The amount approximated 0.5% of the total.

The above curve was determined spectroscopically with the Beckman quartz spectrophotometer at a wave length of 320 mμ. It follows that the curve derived can have a meaning in terms of percentage only if all the material present in each of the tubes has an identical extinction coefficient. This was checked experimentally for several of the tubes of the main band and a recovery obtained approximating 97% calculated on the basis of the initial weight taken. There was barely sufficient of the 0.5% impurity to check the extinction coefficient and to show that it had the 4-aminoquinoline type of absorption. A further point to be checked was whether or not a homogeneous curve would be obtained with an

entirely different system. Isopropyl ether–buffer was therefore studied and found to give a similar result. In summation of the several results, it would appear that the probability was slight of there being present impurity greater than about 0.5% for this particular preparation.

In a similar study on a sample of 7618 which was somewhat less pure, the solubility method revealed 1.5% impurity, as shown in Figure 3. The distribution method gave the result shown in Figure 4. A buffer somewhat less concentrated was used for this run and the partition coefficient was correspondingly higher. Here 2.6% of impurity was revealed, nearly double that revealed by the solubility method. In this case, a crystalline picrate of the impurity was prepared and found to have a different carbon content than that from the main band. The picrate from tube 9 converted to the picrate with two equivalents of picric acid in acetone melted at about 117°, then resolidified and melted sharply at 210–11° C. ($C_{30}H_{32}ClO_{14}N_9$: Calculated, C 46.35, H 4.15; found, C 46.45, H 4.28). The picrate prepared in the same way from tubes 16 to 19 gave a poor melting point, finally melting at 158–63° C. (C 48.05, H 4.34).

Other antimalarials including atabrine were studied by both methods as the work progressed and opportunity for comparison was given. In all cases at hand, the countercurrent method has revealed an amount of impurity nearly double that shown by the solubility method. This would in all probability usually hold true except where either part or all of the impurity had a partition ratio very similar to the substance of interest. The probability of this occurring may be considerable or slight, depending on the type of system used and the type of compound investigated. As has been pointed out (2), the partition ratio is a highly specific constant if the free base has a large organic phase–aqueous phase partition coefficient, but by the addition of buffer to the aqueous phase, the over-all relative amounts in the two phases are shifted so that they are about equal in amount. In this way the effect of the dissociation constant of the base is incorporated into the effective partition ratio.

The partition ratio of 7618 shifts with change of pH, as shown in Figure 5, for approximately 2 molar phosphate buffer and chloroform. For comparison with the chloroform system the reciprocal of the partition ratio of quinine in the system isoamyl alcohol–2 molar citrate is given. The slope of the latter curve is much more gradual and much of the advantage of the use of the buffer is lost. In support of this, practically always relatively large differences in partition ratios were found for the closely related synthetic antimalarials in the chloroform system, but comparatively small differences in the partition ratios of the various cinchona alkaloids in the isoamyl alcohol system were found. In the latter case, the phosphate probably has appreciable solubility in the butanol phase.

After a sufficient number of samples of antimalarials were studied by both the solubility method and the distribution method so that complete confidence in the latter method was warranted, it was used almost exclusively. The distribution method was the one of choice because of the greatly reduced time required
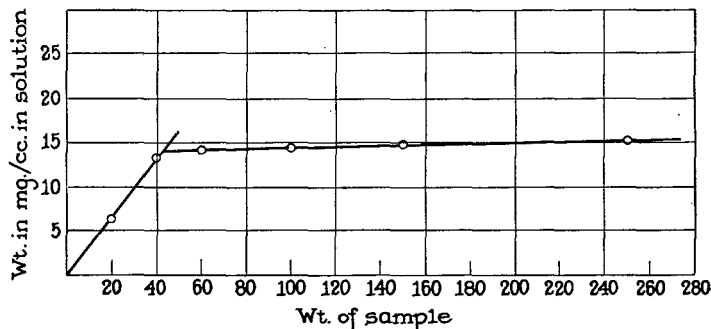
Figure 3.   Solubility Curve of Sample 2 of 7618
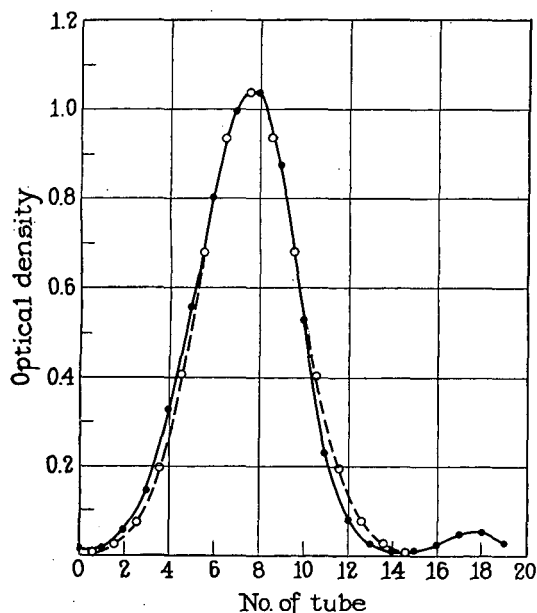
Figure 4. Countercurrent Distribution Pattern of Sample 2 of 7618

for a determination and also because of the ready ease with which an impurity could be isolated by simple evaporation of the tubes containing the impurity and then further characterized.

PLASMOCHIN INVESTIGATIONS

Experience with plasmochin, Formula II, will serve to show the manner of investigation for drugs less pure than 7618 and atabrine. However, the examples given in this paper in no way indicate the purity of the synthetic antimalarials to be found on the market today. Preliminary investigation of partition ratios
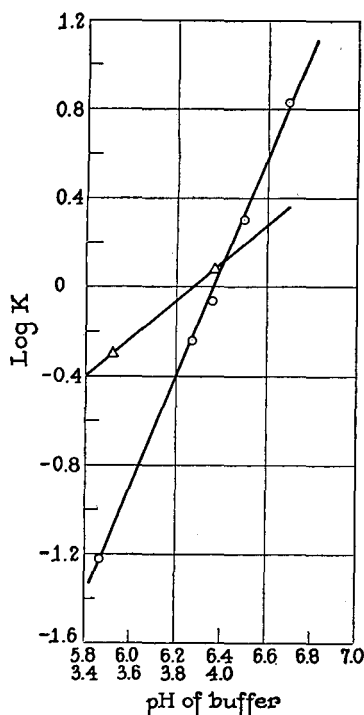
suggested a system in which cyclohexane or isopropyl ether was the upper phase and 2.1 molar phosphate buffer at pH 5.33 was the lower phase. The partition ratio showed a shift with concentration but was near the optimum value of 1.

II
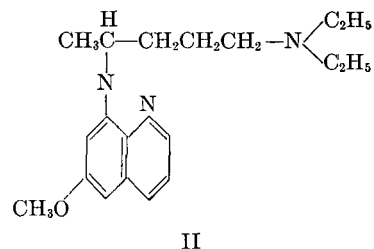
The sample used for the first determination was satisfactory from the analytical standpoint and had been several times recrystallized as the hydriodide. There seemed reason to believe it of high purity from the conventional standpoint at the time. When converted to the citrate, a derivative first reported by Leslie Hellerman in an Office of Scientific Research and Development contract report, it melted at 126–128° C. and gave the correct analytical figures for carbon and hydrogen. Repeated recrystallization did not appreciably change the melting point. A 19-transfer distribution gave the result shown in Figure 6. The relative amount present in each tube is shown by the extinction at 370 mμ. The deviation from the calculated curve (13) is plainly shown.

The deviation apparent at tubes 15 to 19 was further supported by determination of partition coefficients of the material present in these tubes and comparison with that in tubes 9 to 11. The material in the former proved to have a partition coefficient roughly three times that of the latter, which were presumably the pure plasmochin fractions. Although a rough appraisal of the amount of impurity could be estimated from this distribution, a second distribution was made in order to make a more accurate estimate. For this purpose the material in tubes 15 to 19 was combined and redistributed in the same system. This gave the curve shown in Figure 7. From this distribution and the calculated curves of the two components the amount of impurity in the original can be estimated to approximately ±1.0%. On the other hand, material isolated from tube 11 of Figure 6 gave the theoretical curve for a pure substance (13).

A citrate prepared from tubes 15 and 16 of Figure 7 melted at 136–139°, whereas a citrate prepared from tube 12 of Figure 6 melted at 126–128° C. A mixture of the two melted at 118–133° C. Subsequently it was shown by synthetic studies (5) that the higher melting substance was an isomer of plasmochin, possibly Formula III:

Figure 5. Effect of Change of pH of Buffer on Partition Ratio

⊙ = 7618, △ = quinine
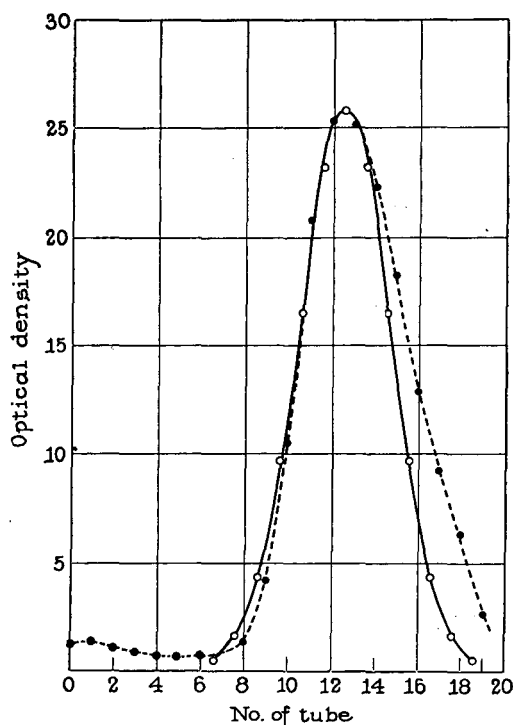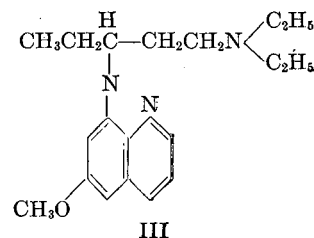
Figure 6. Countercurrent Distribution Pattern of a Plasmochin Sample

III

It was further of interest at the time to investigate the purity in the same way of a sample of the older commercial plasmochin of German make (Figure 8). Approximately double the amount of the so-called isomer is shown and also several per cent of other impurities. These were not further investigated.

At the conclusion of these studies it became desirable to obtain a sufficient amount of the pure plasmochin for clinical study, since one of the basic objections to plasmochin had always been its inherent toxicity. Attempts were accordingly made in several laboratories to remove the isomer by recrystallization of its salts and by distillation. These attempts were unsuccessful. In one case the citrate recrystallized four times from different solvents (by Hellerman) gave as much deviation or slightly more than the original sample when it was investigated by the distribution method.
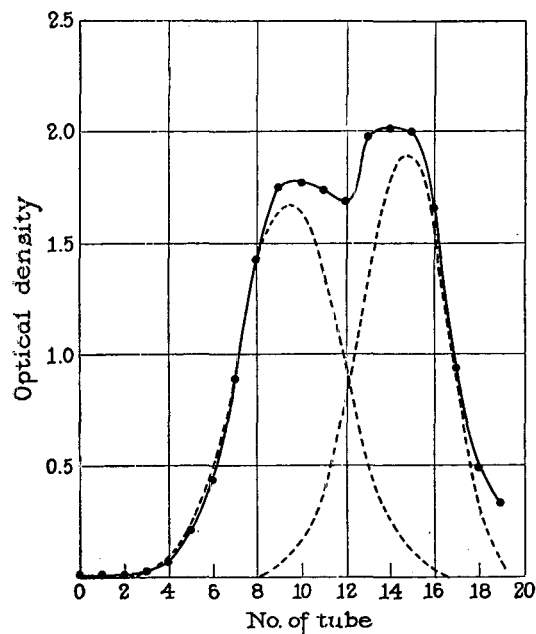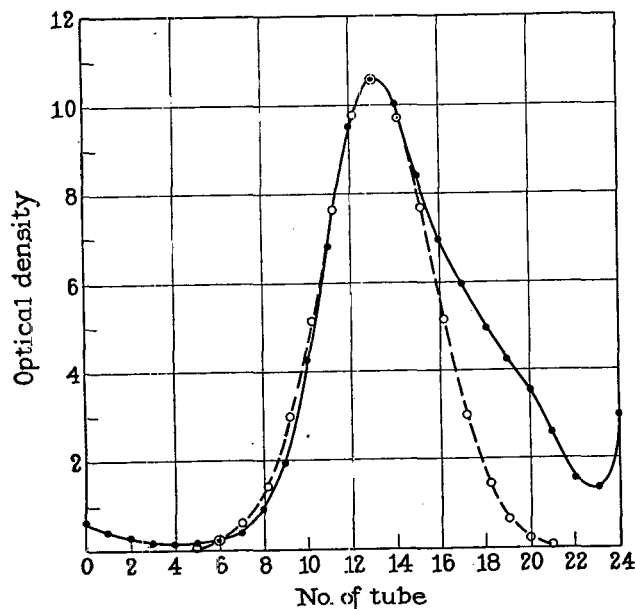
The most certain method of removing the isomer then appeared to be the distribution method itself with isopropyl ether. An attempt was therefore made to employ the separatory funnel technique (2), which permitted the use of much larger volumes of both phases than was possible in the distribution machine. An 8-transfer distribution employing 1800 cc. of each phase gave the result shown in Figure 9. The weight of free base recovered from each tube is shown. The material in tubes 6 to 8 was combined and converted to the citrate ($C_{25}H_{37}O_8N_3$: Calculated, C 59.25, H 7.37; found, C 59.03, H 7.33). This material gave a "pure" curve (13) when tested by the distribution method.

At the same time it was of interest to isolate a certain amount of the isomeric impurity for identification and further study. This presented a more difficult problem in view of its small percentage, but it was done mostly by the separatory funnel technique. Fractions 0 to 2 from four separate runs made as in Figure 9 were combined and redistributed. Again the same tubes were combined and redistributed. At this point the same three tubes had become nearly pure isomer, as demonstrated by a final purification made with the machine. The citrate obtained in this way melted at 136–139° C. (C 59.00, H 7.22).

CONCLUSIONS

It is apparent that countercurrent distribution is an especially useful tool for proving purity with basic substances like the synthetic antimalarials. This was further substantiated by the routine investigation of well over a hundred preparations of different synthetic antimalarials. The method requires only a small sample, does not require great length of time, and gives quantitative results. The final point of question, however, is its reliability in demonstrating the absence of impurity. As with all methods of proving purity, this question cannot be answered in the sense of the absolute but only as an estimated probability. In regard to the present method, this question resolves itself into an estimate of the probability that any impurity might have a partition ratio near enough that of the substance itself to escape detection. When it is possible to employ systems which give a large shift of partition coefficient with change of pH as in Figure

Figure 7. Pattern Obtained on Redistributing Inhomogeneous Tubes from Figure 6

Figure 8. Countercurrent Distribution Pattern of an Older Commercial Sample of Plasmochin
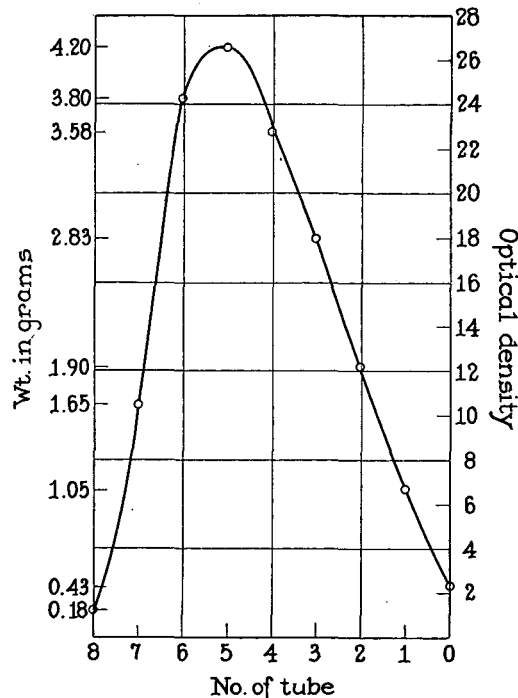
Figure 9. Separatory Funnel Countercurrent Distribution of Plasmochin

5, the probability of identical partition ratios is small. It becomes very much less if a second or third entirely different system gives a perfect distribution and especially when the more conventional criteria are also all in good agreement. The method by no means replaces or minimizes the need for the use of the older more conventional approach, even though it will be found much more decisive for many cases.

When the limitations of the method are properly understood, a countercurrent distribution pattern, such as those in this paper, gives an especially informative picture from the standpoint of identification. It can be used for this purpose as a physical constant, since the partition ratio for the phase pair employed can be easily calculated (13). Moreover, certain other characteristic properties can also be deduced, such as the degree of adherence to or deviation from a constant partition ratio at a given concentration level. Further, the purity of the sample employed is usually at once apparent and the characteristic partition ratio can be accurately derived, even though the sample used was not pure.

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Mass Spectrometer–Hydrochlorination Analysis of Butenes

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To improve the accuracy of determining individual butenes, isobutene is converted to tert-butyl chloride prior to mass spectrometer analysis. Two special methods of computation have been devised, modifications of the basic principles of analyses proposed by Washburn, Wiley, and Rock.

THE application of the mass spectrometer to the analysis of hydrocarbon mixtures consisting essentially of C_4 paraffins and olefins has been discussed in detail by Washburn, Wiley, and Rock (3). While such analyses show commendable accuracy for the paraffin constituents in the mixture, the determination of olefins is accomplished with a lesser degree of certainty. Because of the marked similarity of the butene spectra, the resolution of the butenes is greatly influenced by the stability of the instrument and the presence of small concentrations of C_5 and higher olefins.

In order to improve the accuracy with which individual butenes may be determined, the authors have developed a procedure whereby isobutene is converted to tert-butyl chloride prior to mass spectrometer analysis. This reduces the number of butene mass isomers in the mixture from three to two, thus simplifying the resolution of the remaining 1- and 2-butenes. The isobutene is determined as tert-butyl chloride. Analysis of butane-butene fractions by this method has proved to be considerably more reliable for isobutene than samples analyzed in the conventional manner. The geometrical isomers cis-2-butene and trans-2-butene have nearly identical mass spectra and are usually grouped in the computation of routine analyses. In the event butadiene is present in the sample, no difficulty is encountered by the prescribed procedure, since the diolefin does not react with hydrogen chloride. The concentration of butadiene is determined accurately in the conventional manner (1).

The advantages gained by conversion of isobutene to tert-butyl chloride become readily apparent on consideration of the mass spectra of the individual components. Thus in Figure 1 the similarity of the spectra of isobutene, 1-butene, and 2-butene is shown, as compared with isobutane, n-butane, hydrogen chloride, and tert-butyl chloride. The over-all difference between the mass spectra of a typical butane-butene mixture before and after hydrogen chloride treatment is shown in Figure 2. Of primary importance in the hydrogen chloride–treated sample record is the noticeable reduction of the mass 56 peak due to removal of isobutene and the appearance of relatively large peaks at masses 57 and 77, indicating the presence of tert-butyl chloride.

It was determined from the analyses of a number of plant streams that no serious interference is encountered in resolving mixtures containing less than approximately 3 mole % of pentenes. Higher concentrations of pentenes contribute significantly to the butene mass spectra, thereby increasing the probable error in the butene split. However, the majority of mixtures of practical interest are, or can be made, nearly free of pentenes; hence this limitation is not a serious factor.

Repeated introduction of hydrochlorinated samples containing excess anhydrous hydrogen chloride to the mass spectrometer had no apparent adverse effect on operation of the instrument, since no subsequent change occurred in either the spectrum or sensitivity of calibrating compounds.

PROCEDURE

The method consists essentially of converting isobutene to tert-butyl chloride in the manner described by McMillan (2), wherein the sample is reacted with hydrogen chloride at reduced temperature and pressure.

A measured amount of the sample to be analyzed is placed in a 25-cc. reaction bulb with a known amount of hydrogen chloride
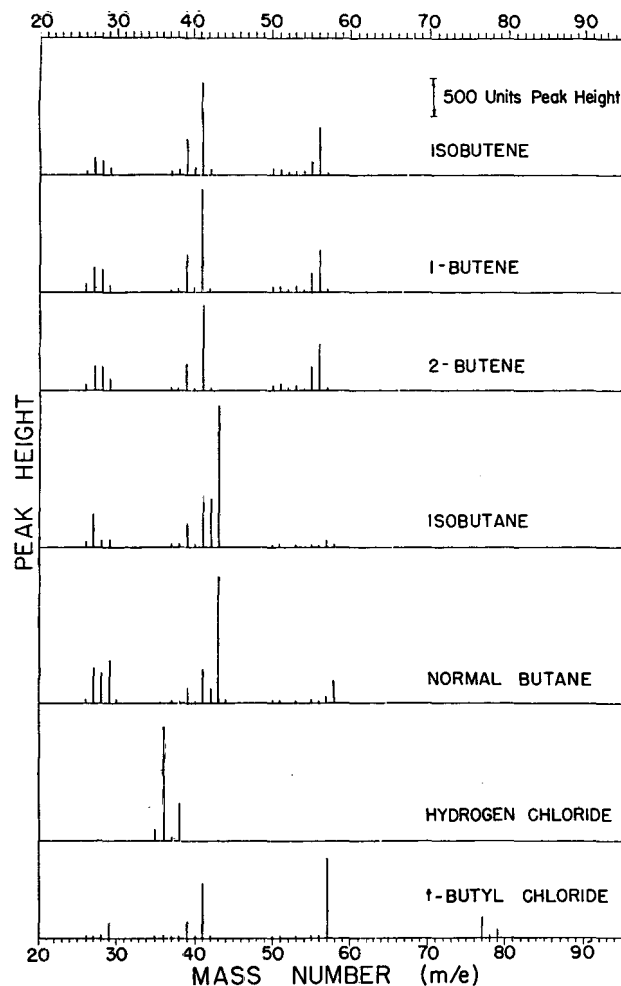
Figure 1. Mass Spectra of Calibrating Compounds at 40-Micron Pressure

gas at room temperature. The relative amounts of sample and hydrogen chloride which are blended together are a function of the isobutene content, since the partial pressure of the relatively high boiling *tert*-butyl chloride at room temperature must not exceed 200 mm. of mercury, its vapor pressure. For samples containing less than 50% isobutene, 300 mm. of sample and 300 mm. of hydrogen chloride gas are blended, while for samples containing more than 50% isobutene, 150 mm. of sample and 300 mm. of hydrogen chloride are used. The reaction bulb is then alternately cooled with a suitable refrigerant such as liquid nitrogen to condense the sample hydrogen chloride mixture, and warmed to vaporize partially the contents in the bulb. Usually three cycles of cooling and warming are sufficient to complete the reaction and the final warming operation brings the reaction bulb to room temperature. Under these conditions the reaction is quantitative and the *tert*-butyl chloride is completely vaporized. This reaction mixture containing excess hydrogen chloride is then ready to be introduced to the mass spectrometer.

COMPUTATION

The first mass spectrum is obtained from the original untreated sample. In subsequent discussion this record is referred to as record A. The second mass spectrum is then determined for the hydrogen chloride–treated sample, which is designated as record B. In order to achieve maximum accuracy in analyses of this nature, two special methods of computation have been devised according to the type of analysis wanted. These methods, outlined below, are modifications of the basic principles of analyses as proposed by Washburn, Wiley, and Rock (*3*).

Method 1. This procedure is recommended for C_1 to C_4 samples where an analysis of isobutene and the sum of the *n*-butenes are sought.

1. The over-all composition of the sample is first computed in the conventional manner from record A with all the butenes calculated together as a group.
2. Record B is employed only to determine the concentration of isobutene relative to the *n*-butenes. This may be done by calculating isobutene in terms of *tert*-butyl chloride using mass 77, and the *n*-butenes by means of mass 56 after subtracting contributions due to other components in the mixture. The analysis of isobutene and *n*-butenes is then obtained by applying this ratio of isobutene to *n*-butenes to the total butene concentration calculated from record A in step 1.

In order to calculate more accurately the residual peak height at mass 56 it is advisable to apply the isobutane–*n*-butane concentrations as calculated in step 1 from record A to the computation of record B. The two records may be directly related by comparing the mass 43 peaks, thereby determining accurate isobutane–*n*-butane contributions to mass 56 peak in record B.

Method 2. This procedure is recommended for C_1 to C_4 samples where an analysis of isobutene, 1-butene, and 2-butenes (*cis* and *trans* isomers being grouped) is sought.

1. Record A is used only to calculate the analysis of propane, isobutane, and *n*-butane by the conventional method.
2. The concentrations of propane and the butanes are applied to record B by comparing the 43 peaks of the two records (similar to Method 1, step 2, above). Contributions of propane and the butanes to the propene, butene (and butadiene, if present) mass peaks may then be subtracted from the observed peak heights.
3. Isobutene is determined from the mass 77 peak in record B.
4. Propene is calculated as a monoisotopic residual 42 peak in record B.
5. 1-Butene and 2-butenes are determined by solving two simultaneous equations based on the residual 39 and 56 peaks (or 41 and 56 peaks).
6. The complete composition may be calculated from the above data in the usual manner.

Pentanes, if present in the mixture, are calculated in the same manner as the butanes. It was verified experimentally that 2-methyl-1-butene and 2-methyl-2-butene react with hydrogen chloride at low temperature to form *tert*-amyl chloride, while the other pentenes do not react. No serious interference results from this reaction because mass 91 peak defines the amount of *tert*-amyl chloride present. The unreacted pentenes are calculated by means of the residual mass 70 peak. Attempts to extend this hydrogen chloride treatment method to pentane-pentene mixtures for a more accurate resolution of the pentenes are now in progress.

When it was desirable to confirm the fact that isobutene had

Table I. Analysis of Phillips Synthetic Mixture 4

Component	Known Composition	M.S. Analysis, HCl Treatment	Difference
		Mole Per Cent	
Ethane	0.02	0.0	−0.02
Propane	3.25	3.2	−0.1
1,3-Butadiene	2.58	2.4	−0.2
Isobutene	44.82	45.0	+0.2
1-Butene	12.20	11.5	−0.7
2-Butene	12.24	13.2	+1.0
Isobutane	11.23	11.6	+0.4
n-Butane	11.25	10.6	−0.6
Isopentane	1.20	1.3	+0.1
n-Pentane	1.21	1.2	0.0
Total	100.0	100.0	...

Table II. Analysis of Phillips Synthetic Mixture 8

Component	Known Composition	M.S. Analysis, HCl Treatment	Difference
		Mole Per Cent	
Propene	8.2	8.1	−0.1
Propane	8.8	9.1	+0.3
Isobutene	5.1	5.0	−0.1
1-Butene	9.6	9.1	−0.5
2-Butene	6.2	6.8	+0.6
Isobutane	12.3	12.0	−0.3
n-Butane	31.6	32.0	+0.4
Isopentane	8.6	8.5	−0.1
n-Pentane	9.6	9.4	−0.2
Total	100.0	100.0	...

Table III. Mass Spectra of tert-Butyl Chloride and tert-Amyl Chloride

Mass	tert-Butyl Chloride	tert-Amyl Chloride
26	8.38	39.4
27	4.78	300
28	11.2	41.2
29	75.6	216
35	2.64	10.9
36	6.03	47.0
37	6.43	13.6
38	13.3	41.0
39	73.0	268
40	10.8	39.6
41	199	491
42	12.6	102
43	1.0	465
50	4.90	15.1
51	7.03	31.5
52	1.20	8.80
53	4.17	54.4
54	1.18	13.0
55	10.2	447
56	17.3	28.5
57	301	5.69
69	0.06	20.1
70	0.07	101
71	0.07	614
72	0.09	31.5
73	0.54	2.82
74	0.07	0.12
75	1.09	5.63
76	7.75	358
77	100	567
78	5.28	130
79	32.0	181
91	0.04	100
92	0.04	7.75
93	0.03	32.0
106		1.58
Sensitivity	20.3	5.12

Sensitivity of n-butane at mass 58 = 10.5.

Table IV. Analysis of Isobutene Mixture by Special Procedure

Hydrocarbon	Mole %	Precision Limits[a] ±
Propene	0.2	0.05
Propane	0.2	0.05
Isobutene	97.8	0.3
1-Butene	0.8	0.1
2-Butene	0.1	0.02
Isobutane	0.2	0.1
n-Butane	0.1	0.0
Pentenes	0.2	0.0
Hexenes	0.1	0.0
Heptenes	0.1	0.0
Diisobutene	0.2	0.0
Total	100.0	

[a] Precision limits based on two separate analyses.

completely reacted with hydrogen chloride, the sum of the mass 53 and 55 peaks due only to butenes was calculated. Since 1-butene and 2-butene mass spectra are essentially equal for this combination of peaks, the mass 56 peak calculated for this residual was found to approximate closely that actually found for the butenes.

The data in Tables I and II compare the known compositions of Phillips synthetic mixtures 4 and 8 with those determined by the present method. Reference to these tables shows that the calculated and known compositions of isobutene, 1-butene, and 2-butene agree to within 0.1 to 1.0 mole %. The mass spectra of tert-butyl and tert-amyl chlorides are tabulated in Table III.

The over-all time requirements for the analysis of C_4 fractions were found to be 2 man-hours by Method 1, and 2.5 man-hours by Method 2. The hydrochlorination procedure consumed about 0.5 hour, while the remainder of the time was spent on mass spectrometer analysis.
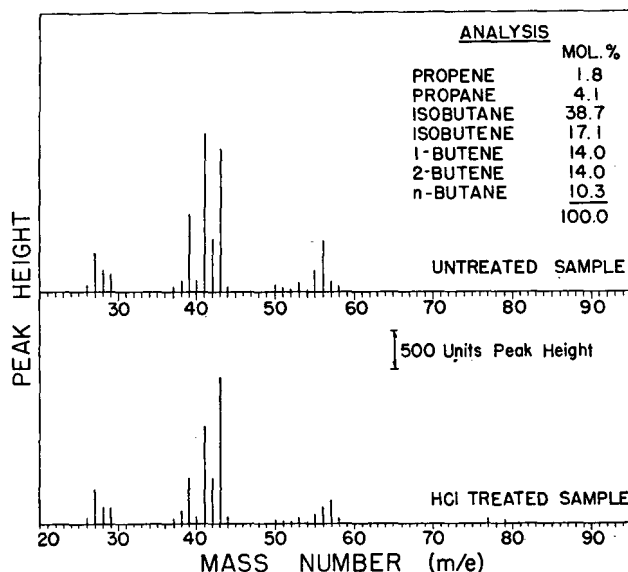
Figure 2. Mass Spectra of Typical BB Feed at 40-Micron Pressure

Table V. Uncertainties in Determination of Each Butene Isomer Due to Presence of Other Butenes

(Conventional M.S. analysis and HCl treatment method)

Uncertainty, microns pressure

Butene Computed	Mass	Untreated Butene Mixture					HCl-Treated Butene Mixture				
		Isobutene	1-Butene	2-Butene	Σm	Root error squared	tert-Butyl chloride	1-Butene	2-Butene	Σm	Root error squared
Isobutene	41	0.0059	0.0060	0.0054	0.0173	..	0	0	0	0	....
	55	0.0353	0.0405	0.0458	0.1216	..	....	....	....	....	....
	56	0.0394	0.0343	0.0405	0.1143	..	0	0	0	0	....
	57	.....	.....	.....	.....	..	0.0100	0	0	0.0100	....
	Σs	0.0806	0.0809	0.0916	0.2531		0.0100	0	0	0.0100	....
		Sensitivity fluctuations				0.15	....	....	....	....	0.01
		Peak fluctuations				0.17	....	....	....	....	0.01
		Total fluctuations				0.22	....	....	....	....	0.01
1-Butene	41	0.0382	0.0391	0.0350	0.1123	..	0.0240	0.0417	0.0374	0.1031	..
	55	0.0153	0.0176	0.0198	0.0527	..	.....	.....	.....	.....	..
	56	0.0535	0.0466	0.0549	0.1550	..	0.0033	0.0317	0.0374	0.0724	..
	57	.....	.....	.....	.....	..	0.0206	0	0	0.0206	..
	Σs	0.1070	0.1032	0.1098	0.3200		0.0480	0.0734	0.0748	0.1962	
		Sensitivity fluctuations				0.19	....	....	....	....	0.12
		Peak fluctuations				0.20	....	....	....	....	0.13
		Total fluctuations				0.27	....	....	....	....	0.17
2-Butene	41	0.0381	0.0390	0.0349	0.1120	..	0.0240	0.0354	0.0317	0.0874	..
	55	0.0214	0.0246	0.0277	0.0737	..	.....	.....	.....	.....	..
	56	0.0167	0.0145	0.0171	0.0484	..	0.0037	0.0353	0.0417	0.0808	..
	57	.....	.....	.....	.....	..	0.0166	0	0	0.0166	..
	Σs	0.0762	0.0781	0.0798	0.2341		0.0407	0.0707	0.0734	0.1848	
		Sensitivity fluctuations				0.13	....	....	....	....	0.11
		Peak fluctuations				0.14	....	....	....	....	0.12
		Total fluctuations				0.20	....	....	....	....	0.16

Butene mixtures contained 1 micron of each butene.

n-BUTENE ANALYSIS IN ISOBUTENE SAMPLES

In special cases it is desired to determine a 1-butene and 2-butene split for samples containing approximately 95% isobutene. Although the hydrogen chloride treatment described eliminates isobutene as such, the resulting *tert*-butyl chloride interferes seriously in the resolution of the small concentration of 1-butene and 2-butene.

To increase the relative partial pressure of 1-butene and 2-butene compared to the partial pressure of *tert*-butyl chloride in the hydrogen chloride–treated sample, a simple partial condensation is made by cooling the reaction bulb to −40° C. prior to introduction to the mass spectrometer. At the reduced temperature and pressure existing in the reaction bulb practically all of the *tert*-butyl chloride is condensed while only a relatively small amount of the butenes is dissolved by the liquid phase. It was found that this process increased the butene concentration in the vapor phase by a factor of about 10. A sample may then be removed from the reaction bulb at −40° C. and introduced directly into the mass spectrometer.

The mass spectrum which is obtained from the vapor in the reaction bulb at −40° C. (record C) is used in conjunction with the two mass spectra already described from the untreated sample and the hydrogen chloride–treated gas sample for computation of the analysis. Records A and B are computed in the manner outlined in Method 2, with the exception that the more stable 57 peak is used as the base peak for *tert*-butyl chloride instead of the 77 peak. Record C is used only to indicate the relative amounts of 1-butene and 2-butenes by solving two simultaneous equations based on the 39 and 56 peaks. This ratio may then be applied to the results calculated from records A and B to complete the analysis.

A typical analysis of a sample containing more than 95% isobutene which was treated by this latter method is shown in Table IV.

ACCURACY OF METHOD

To determine what advantage the method might have in reducing errors due to changes in sensitivity caused by fluctuations of the instrument, a mathematical analysis was made of a representative mixture. Error breakdowns, calculated by an inverse method (1) for an assumed sensitivity fluctuation of 1% are shown in Table V. It is apparent that the uncertainties for a mixture containing *tert*-butyl chloride are smaller than for the mixture in which isobutene is present; hence greater accuracy should result from the use of hydrogen chloride treatment than would be possible from the conventional mass spectrometer analysis.

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Determination of Sodium, Potassium, Aluminum, and Zinc

In Derivatives of Carboxymethylcellulose

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Methods are described for the determination of sodium, potassium, aluminum, and zinc in derivatives of carboxymethylcellulose. They were developed on the basis of accuracy and rapidity of analysis for the application to research and control purposes.

THE rapidly increasing commercial importance of the metallic salts of carboxymethylcellulose makes desirable the development of analytical methods for the accurate determination of the specific metal ions contained therein. Procedures have been devised for the determination of sodium, potassium, aluminum, and zinc in their respective salts of carboxymethylcellulose. Most of the methods presented in this paper are satisfactory for the analysis of varying amounts of one element in the presence of the other elements mentioned. For example, small amounts of sodium are likely to be found in other salts of carboxymethylcellulose and it would be useful to analyze for sodium and aluminum in a mixture of the sodium and aluminum salts of carboxymethylcellulose.

In so far as possible, rapid methods of analysis have been developed, utilizing colorimetric and volumetric techniques.

Considerable investigation was required to find a suitable rapid method for the digestion of the salts of carboxymethylcellulose, in order that the cellulosic residue might be destroyed and leave the metallic constituents in a soluble state. Wet-ashing with a sulfuric acid–nitric acid mixture is commonly used for the digestion of organic material and is satisfactory for this type of

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product, but it is time-consuming. Lindner (8, 9) and others (3) have reported that 30% hydrogen peroxide aids in the digestion of plant tissue. The use of 30% hydrogen peroxide subsequent to a preliminary treatment with sulfuric acid greatly speeds up the digestion process.

Dry-ashing for the destruction of cellulose residues is usually more rapid than wet-digestion but suffers from the fact that at elevated temperatures insoluble oxides may be formed with some metals, which gives low analytical results. This difficulty may be overcome and most of the benefits of dry-ashing retained by ashing at some moderate temperature such as 400° C. The ashing of the sample should be only partially completed and at a moderate temperature it should be sufficient to remove all of the volatile constituents and to reduce the bulk of the original sample to a carbonaceous residue. Subsequent to dry-ashing, the residue is taken up in concentrated sulfuric acid with continued additions of 30% hydrogen peroxide until the solution becomes clear. When digestion is complete, the clear liquid remaining in the calibrated 50-ml. Kjeldahl digestion flask (Figure 1) is diluted to the mark with distilled water and suitable aliquots are removed for metal analysis by the various procedures described below. When it is known that sodium is present alone in an organic compound, a convenient method of analysis (7) is to

evaporate the sample with sulfuric acid and weigh as the sulfate. Sodium can be determined in the presence of other metals directly as the triple salt (*1*, *13*), sodium magnesium uranyl acetate. Potassium present in amounts up to ten times the amount of sodium does not interfere. Moderate amounts of magnesium, ammonium, calcium, barium, strontium, ferric, aluminum, chromium, zinc, and many other metal·ions can be tolerated.

Two methods are presented for the determination of aluminum, one a gravimetric procedure in which the aluminum is precipitated with 8-hydroxyquinoline (*6*) and the other a colorimetric method (*11*) involving the use of ammonium aurintricarboxylate (Aluminon) to form a red colored complex. The 8-hydroxyquinoline procedure is well established and reliable, but time-consuming. The authors have modified the colorimetric Aluminon method from a procedure which was designed for trace amounts to one which gives satisfactory results on samples ranging up to 12% aluminum. This is both rapid and convenient to carry out.

Figure 1. Kjeldahl Flask

Potassium is a rather difficult element to determine. The two common methods, both slow and tedious, involve precipitation of potassium as the chloroplatinate and the perchlorate. In 1941 Willard and Boyle (*12*) developed a method in which potassium is quantitatively precipitated as the periodate. This precipitate is dissolved in a boric acid–borax buffer, potassium iodide is added, and the resulting free iodine is titrated with standard arsenite solution. Potassium may be separated from aluminum, zinc, sodium, and calcium by this scheme of analysis. It is possible to separate as little as 0.4 mg. of potassium from seventy times as much sodium. This procedure has been adapted to the wet-ashing technique and has proved both rapid and accurate for determining potassium in carboxymethylcellulose.

Zinc is easily determined in carboxymethylcellulose by reaction with a standard solution of potassium ferrocyanide to form potassium zinc ferrocyanide:

$$2 K_4Fe(CN)_6 + 3 Zn^{++} \longrightarrow K_2Zn_3 [Fe(CN)_6]_2 + 6K^+$$
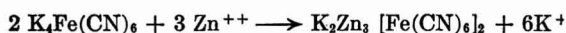
SPECIAL REAGENTS

All reagents are of reagent grade unless otherwise noted.

Determination of Sodium by Magnesium Uranyl Acetate Procedure. It is best to make magnesium uranyl acetate up in 4-liter quantities, since such a large amount is used. Dissolve 1200 grams of magnesium acetate tetrahydrate or 800 grams of anhydrous magnesium acetate and 120 grams of glacial acetic acid in distilled water and dilute to 2 liters. Heat on a hot plate to dissolve, stirring occasionally to promote solution. Prepare another solution by dissolving 180 grams of uranyl acetate dihydrate and 120 grams of glacial acetic acid in distilled water, dilute to 2 liters, and heat until in solution. Mix the two solutions, cool to 18° to 20° C. and hold there 1.5 to 2 hours. The solution should be cloudy with some precipitate. If clear, add 25 ml. of distilled water containing 1 gram of c.p. sodium chloride to form precipitate. Filter through a large funnel, using 32-cm. fluted filter paper. When paper clogs and filtration slows too much,
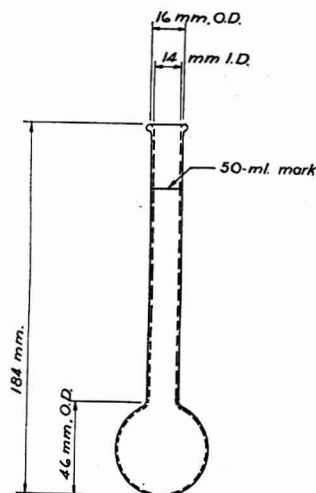
change filter papers. Keep the beaker below 20° C., preferably at 18° C., and do not allow solution in funnel to become too warm.

Sodium Wash Solution. Mix 35 ml. of glacial acetic acid, 405 ml. of absolute ethyl acetate, and 460 ml. of absolute ethanol. Add magnesium uranyl acetate reagent to this until a precipitate forms at 20° C. Filter.

Preparation of Jones Reductor. To 300 grams of pure 20- to 30-mesh zinc add 300 ml. of 2% mercuric nitrate (or chloride) and 1 to 2 ml. of concentrated nitric acid. Stir thoroughly for 5 to 10 minutes, decant solution, and wash 2 to 3 times by decantation Fill the reductor tube with distilled water, and add zinc slowly until column is completely packed. Wash with 500 ml. of distilled water, using gentle suction; leave reductor full of water after washing. The level of liquid should never drop below the zinc. Before adding zinc, place a plug of glass wool in reductor to prevent zinc from plugging the stopcock. Place another plug at top weighted with glass beads to keep zinc well packed. These columns will last for several months with reasonable care. In time the zinc dissolves and must be replaced.

Diphenylamine Indicator. Dissolve 1 gram of diphenylamine in 99 grams of concentrated sulfuric acid. Keep in a dark-colored dropping bottle.

Determination of Aluminum by 8-Hydroxyquinoline Procedure. Dissolve 50 grams of 8-hydroxyquinoline in 880 ml. of distilled water and 120 ml. of glacial acetic acid. Agitate to ensure solution, and filter into a dark bottle. This reagent is good for 2 weeks, after which it should be discarded.

ALUMINON COLORIMETRIC PROCEDURE

Aluminon Solution, 0.2%. Dissolve 0.2 gram of ammonium aurintricarboxylate in 100 ml. of distilled water.

Standard Aluminum Solution. Dissolve 1.0000 gram of pure aluminum metal in dilute hydrochloric acid and dilute to 1 liter.

Working Standard. Dilute 5 ml. of the standard to 500 ml. (1 ml. = 0.01 mg. of aluminum).

Determination of Potassium. Aldehyde-Free Ethanol. Reflux 95% ethanol 2 to 3 hours after adding 0.5 gram of sodium hydroxide and 2.5 grams of silver nitrate per liter. Distill.

Anhydrous Ethyl Acetate. Add magnesium perchlorate to 99% ethyl acetate and distill. Add equal parts of the ethanol and the ethyl acetate for the reagent.

Periodic Acid. Dissolve 1 gram of periodic acid in 3 ml. of water just before use.

Boric Acid–Borax Buffer. Dissolve 40 grams of boric acid and 40 grams of sodium tetraborate in 1 liter of distilled water.

Determination of Zinc. Potassium Ferrocyanide, $K_4Fe(CN)_6$. Dissolve 80 grams of potassium ferrocyanide analytical reagent in 100 ml. of distilled water and heat on a hot plate until solution is complete. Filter rapidly through a Büchner funnel, using medium filter paper, to remove insoluble residue from the reagent. Transfer immediately to a beaker and cool with occasional stirring. Complete cooling in an ice bath, stirring to assure small crystals. Filter through Büchner funnel. Wash with 2 to 3 10-ml. portions of distilled water at least as cold as the sample and preferably colder to prevent too great a loss of precipitate. Transfer the precipitate to a large watch glass, spreading it thin, cover with another glass, and dry in 105° C. oven for 3 to 4 hours. This yields anhydrous potassium ferrocyanide.

To prepare the reagent dissolve 18.78 grams in distilled water and dilute to 1 liter. Standardize against zinc standard until four to six samples are tested. All should fall within a few tenths of a milligram of another.

Procedure for Standardizing. Pipet 20-ml. aliquots of the zinc standard into a 400-ml. beaker. Make up six samples. To the standard add 100 ml. of distilled water, 2 grams of ammonium sulfate, 3 drops of diphenylamine indicator, 5 drops of 1% aqueous potassium ferricyanide, and 15 to 20 ml. of 6 *N* sulfuric acid. Titrate to a green end point, proceeding very slowly with constant agitation near end point. If the end point is passed, back-titrate with zinc standard to first permanent blue coloration. Note temperature of potassium ferrocyanide and milliliters necessary. Make the six runs. Determine the mean, and divide milliliters of titration into 0.005 × ml. of zinc standard for calculating the factor.

Preparation of Zinc Standard. Weigh out 2.500 grams of powdered zinc (reagent grade), making a correction if necessary for the per cent insoluble in sulfuric acid. Dissolve in 50 ml. of distilled water and sufficient concentrated c.p. sulfuric acid to allow the reaction to proceed smoothly but not too rapidly to completion. When all zinc is in solution, dilute to 500 ml.

Diphenylamine Indicator, same as in sodium determination.

ANALYTICAL CHEMISTRY

Table I. Recovery of Potassium and Zinc Added to Sodium Carboxymethylcellulose

(0.25 gram of sodium carboxymethylcellulose digested)

Potassium or Zinc in Sample Mg.	Zinc Added[a] Mg.	Potassium Added[b] Mg.	Found Mg.	Recovered %
None	None	50.0	49.98	99.9
None	None	100.0	99.78	99.8
None	None	150.0	149.96	99.9
None	49.9	None	49.8	99.7
None	99.8	None	99.4	99.6
None	149.7	None	149.7	100.0

[a] Added as ZnCl₂.
[b] Added as KCl.

ANALYTICAL PROCEDURES

Digestion. Weigh into a calibrated Pyrex 50-ml. Kjeldahl flask (Figure 1) a suitable sample of the material to be analyzed, previously dried in an oven at 105° C. for 30 minutes. In the case of a fine powder it is advisable to transfer the weighed sample to the flask in a folded piece of ashless filter paper. Place the flask in an electric muffle furnace at 400° C. for about 20 minutes, remove, and allow to cool. From a buret transfer 5 ml. of concentrated sulfuric acid to the flask, then place on a digestion rack and heat until the reflux is clear (Figure 2). Allow to cool a few minutes and add drop by drop 5 ml. of 30% hydrogen peroxide. Great care should be taken, as the reaction is fast and a large amount of heat is evolved. If allowed to cool to room temperature the reaction is slower. The solution should be clear at this point. Heat to boiling and continue heating until the vigorous boiling ceases. This will drive off the 30% hydrogen peroxide and approximately 2 to 4 ml. of sulfuric acid will remain in the flask.

Determination of Sodium. Gravimetric Procedure. Dry the sample for 30 minutes in an oven at 105° C. to remove moisture. Tare two 30-cc. Vitreosil or platinum crucibles on an analytical balance, and weigh approximately 1 gram of sample into each. Place the crucibles in the muffle furnace at 700° C. for 45 to 60 minutes; a lower temperature or shorter period of time does not remove all carbon, and requires too much sulfuric acid, increasing the possibility of spattering.

After ignition, treat the samples with 4 to 6 ml. of concentrated sulfuric acid, added with a pipet, and evaporate to dryness over a Meker burner or electric heater. The heaters are better for silica crucibles because the even heat reduces the tendency to spatter. The sample should be white at this point, indicating complete conversion to sodium sulfate. If the residue is still black, the treatment with sulfuric acid must be repeated.

Return the crucibles to the muffle furnace at 700° C. for one hour to remove all water of hydration. An hour is sufficient to give constant weight.

Remove the crucibles, place in a desiccator, and weigh when thoroughly cool. About half an hour is necessary to cool Vitreosil crucibles, much less for platinum.

$$\frac{\text{Weight of residue} \times 0.3238 \times 100}{\text{weight of sample}} = \% \text{ sodium}$$

Magnesium Uranyl Acetate Procedure. Digest a 0.2500-gram sample following the directions given under the digestion procedure. Dilute the 2 to 4 ml. of concentrated sulfuric acid remaining in the digestion flask with approximately 20 ml. of water and nearly neutralize the solution with ammonium hydroxide until just acid to methyl orange. Cool and dilute to 50 ml. with distilled water. Mix well and transfer two 10-ml. aliquots to 400-ml. beakers.

Evaporate to 5 to 7 ml. and cool. Pour 150 ml. of magnesium uranyl acetate into each beaker and agitate with variable-speed agitators running at 1500 to 1800 r.p.m. in water baths controlled at 20° ± 1° C. for 45 to 60 minutes. Filter the sample through a Gooch crucible, wash with 30 to 40 ml. of reagent at 20° ± 1° C., and follow with several 3- to 5-ml. washes of wash solution. Dry the crucibles 10 to 15 minutes in a 125° C. oven. On removal, place the crucibles in a filtration flask, wash with small portions of 2 N sulfuric acid until 50 to 75 ml. have been passed, and follow with two to three 5-ml. washes of distilled water. Transfer the filtrate to a 250-ml. beaker, keeping the total volume below 100 ml. if possible. Adjust the acidity to 2 N by addition of 6 N sulfuric acid; 10 ml. will give this normality if 75 ml. of 2 N sulfuric acid were used.

Activate the Jones reductor at this time by the following procedure. Pour 150 ml. of 1 to 20 sulfuric acid by volume through the reductor, using gentle suction. Discard the solution, attach

a clean filtration flask, and pass through the sodium solution at a rate not to exceed 75 ml. per minute. Follow this with three 25-ml. washes of 1 to 20 sulfuric acid and three 25-ml. washes of distilled water. At no time allow the liquid to drop below the top of the zinc. Transfer the solution to an 800-ml. beaker and bubble air through it for 10 to 15 minutes to convert all uranium to the quadrivalent form. Add 15 ml. of 85% phosphoric acid, 40 ml. of 2% aqueous ferric chloride, and 6 to 8 drops of diphenylamine indicator. Titrate with 0.1 N potassium dichromate solution to a permanent purple end point.

$$\text{Ml. of } 0.1 N \text{ K}_2\text{Cr}_2\text{O}_7 \times 0.7666 = \% \text{ sodium}$$

Determination of Aluminum by 8-Hydroxyquinoline Procedure. Digest a 0.5000-gram sample following the directions given under the digestion procedure. Dilute the sulfuric acid remaining in the digestion flask to 30 ml. and transfer to a 400-ml. beaker. Wash the flask several times with distilled water, adding washings to beaker. Add a few drops of methyl orange indicator, and neutralize with ammonium hydroxide until the solution turns yellow and a precipitate forms. Make just acid with concentrated sulfuric acid and dilute to 200 ml.
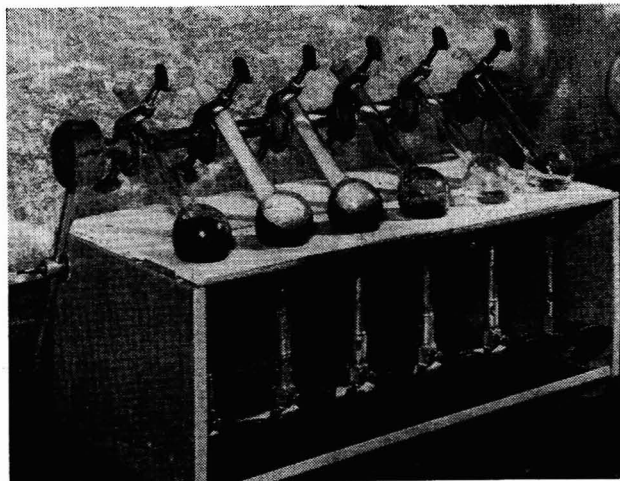
Figure 2. Flasks on Digestion Rack

Heat on a hot plate to 70° C. and add 25 ml. of 8-hydroxyquinoline (oxine) followed by 35 to 45 ml. of ammonium acetate solution, added slowly with stirring to ensure a good precipitate. Turn off the hot plate, but allow samples to remain on the hot plate to digest for 20 to 30 minutes. Tare a 1G3 Jena crucible and filter the precipitate, using considerable suction. Wash six to eight times with 15- to 20-ml. portions of distilled water. Use a policeman to assure transfer of the precipitate. Dry 1.5 hours in a 125° C. oven, cool, and weigh crucibles. To determine per cent aluminum use the following formula:

$$\text{Grams of precipitate} \times 11.746 = \% \text{ Al}$$

ALUMINON COLORIMETRIC PROCEDURE

Digest a 0.2500-gram sample, following the directions given under the digestion procedure. Dilute the sulfuric acid remaining in the digestion flask to 30 ml., cool, and dilute to 50 ml. with distilled water. Mix well and transfer 0.2 ml. to a 25-ml. volumetric flask with a 0.2-ml. serological pipet. Dilute to 10 ml., add 1.00 ml. of 1 to 9 hydrochloric acid and 1.00 ml. of ammonium aurintricarboxylate solution, mix, and add 10 ml. of ammonium acetate solution to adjust the pH to 5.5. Mix, dilute to the mark, and determine the transmittance (I_0/I) after 15 minutes with the Cenco Type B-2 photelometer, using a blank solution as a reference. A green filter is employed. Read per cent aluminum directly from the calibration curve, which is established by determining the transmittancy of various quantities of the working standard, equivalent to 0.02, 0.04, 0.06, 0.08, 0.10, and 0.12 mg. of aluminum.

Determination of Potassium. Digest a 0.500-gram sample following the directions given under the digestion procedure. Boil off the remaining sulfuric acid in the digestion flask and evaporate to dryness. Cool and dissolve the residue in 4 to 5 ml. of 1 to 2 nitric acid and transfer to a 150-ml. beaker. Wash-

Table II. Recovery of Sodium Added to Aluminum Carboxymethylcellulose

(0.25 gram of aluminum carboxymethylcellulose digested)

Sodium in Sample Mg.	Sodium Added[a] Mg.	Total Sodium Mg.	Sodium Found Mg.	Recovered %
0.57	10.00	10.57	10.55	99.8
0.57	10.00	10.57	10.35	97.9
0.57	25.00	25.57	25.50	99.7
0.57	25.00	25.57	25.40	99.3
0.57	50.00	50.57	50.57	100.0
0.57	50.00	50.57	50.50	99.8

[a] Added as NaCl.

Table III. Analysis of Routine Samples of Sodium and Potassium Carboxymethylcellulose

Sample	Gravimetric % Na	Gravimetric % K	Magnesium Uranyl Acetate, % Na	Periodate, % K	Difference, %	Degree of Substitution
S-1	6.09	..	6.09	..	None	0.54
S-2	7.44	..	7.46	..	0.2	0.68
S-3	5.01	..	5.03	..	0.2	0.42
S-4	9.03	..	9.08	..	0.5	0.91
S-5	10.11	..	10.16	..	0.5	1.09
K-1	...	5.73	...	5.69	0.7	0.28
K-2	...	4.82	...	4.80	0.4	0.24
K-3	...	6.78	...	6.74	0.6	0.35
K-4	...	7.58	...	7.55	0.4	0.39

the flask with approximately 3 ml. of water and add the washings to the beaker. Add 3 ml. of water containing 1 gram of periodic acid, stir, allow to precipitate for 3 to 4 minutes, then add 90 ml. of the alcohol–ethyl acetate mixture. Place in an ice bath with mechanical stirring for 30 minutes. Filter through a Gooch crucible and wash with anhydrous ethyl acetate which has been cooled to 0°. Place the crucible and its contents in a 250-ml. beaker, and add 125 ml. of the boric acid–borax buffer solution. The crucible can be left in the solution. When the precipitate has dissolved, add 3 grams of potassium iodide, and titrate the iodine with 0.1 N arsenite solution to a colorless end point.

$$\text{Ml. of } 0.1 \ N \ \text{As}_2\text{O}_3 \times 0.3936 = \% \ K$$

When the amount of potassium is very small (1 to 2 mg.) increase the periodic acid to 1.5 to 2.0 grams. If other metals are not present, decrease the initial volume to 5 ml. Increase time of precipitation to 1.0 to 1.5 hours.

When not more than 70 mg. of sodium are present, the standard procedure is followed. When the sodium is higher, double the volume of alcohol–ethyl acetate mixture; this will separate potassium from as high as 190 mg. of sodium. In the presence of zinc it is best to double the solvent volume.

Determination of Zinc. Digest a 0.5000-gram sample following the directions given under the digestion procedure. Transfer the sulfuric acid remaining in the digestion flask to a 250-ml. beaker, add 15 ml. of 6 N sulfuric acid, and adjust the volume in the beaker to approximately 125 ml. Add 2 grams of ammonium sulfate and 2 to 3 drops of diphenylamine indicator solution.

To determine zinc, titrate with potassium ferrocyanide to a green end point. As the end point fades, the following procedure is necessary. Agitate the solution with a variable-speed agitator at 100 to 200 r.p.m., but no faster. Add zinc from a buret with 2- to 3-inch offset to clear agitator. The solution is colorless before addition of ferrocyanide, forms a Prussian blue fading to green near the end point, then returns to blue. When the end point is reached the green remains without fading. If the end point is passed add standard zinc solution from a volumetric 2-ml. pipet, then titrate to the green end point. Proceed very slowly, adding no more than 0.1 ml. or the end point will be passed. Calculate for per cent zinc by the following formula:

$$\frac{\text{Ml. of } K_4\text{Fe(CN)}_6 \times \text{calculated factor} \times 100}{\text{weight of sample}} = \% \ Zn$$

The factor should be approximately 0.0051 to 0.0053.

DISCUSSION

The reliability of the foregoing procedures was first tested by the recovery of known amounts of potassium, sodium, and zinc added to carboxymethylcellulose. Table I shows results obtained by adding known amounts of potassium as potassium chloride to 0.25 gram of sodium carboxymethylcellulose. The mixture

was carried through the wet-digestion procedure and the potassium determined by the periodate method. In the same manner known amounts of zinc chloride were added to a 0.25-gram sample of sodium carboxymethylcellulose and the zinc was determined by titrating with potassium ferrocyanide. These results indicate that excellent recoveries of the above elements can be made in the presence of sodium.

Table II shows the excellent recovery obtained in the analysis of aluminum carboxymethylcellulose containing added sodium. Sodium chloride was added to 0.25 gram of the aluminum salt, the mixture digested, and sodium determined by the magnesium uranyl acetate method.

In the magnesium uranyl acetate method for the determination of sodium, the sodium is usually precipitated and weighed as sodium magnesium uranyl acetate, a precipitate which is easily decomposed unless carefully dried. A rapid volumetric method has been produced by dissolving this precipitate in dilute sulfuric acid, then pouring the solution through a Jones reductor to reduce the uranium in the compound from hexavalent to a combination of tri- and quadrivalent ions. Since the ratio of sodium to uranium is constant in $\text{NaMg(UO}_2)_3(\text{CH}_3\text{COO})_9.6.5\text{-H}_2\text{O}$, the sodium can be obtained by determination of the uranium. The quadrivalent uranyl ion reacts with potassium dichromate in the following manner:

$$3 \ UO^{++} + Cr_2O_7^- + 8 \ H^+ \longrightarrow 3 \ UO_2^{++} + 2 \ Cr^{+++} + 4H_2O$$

% Sodium and Potassium
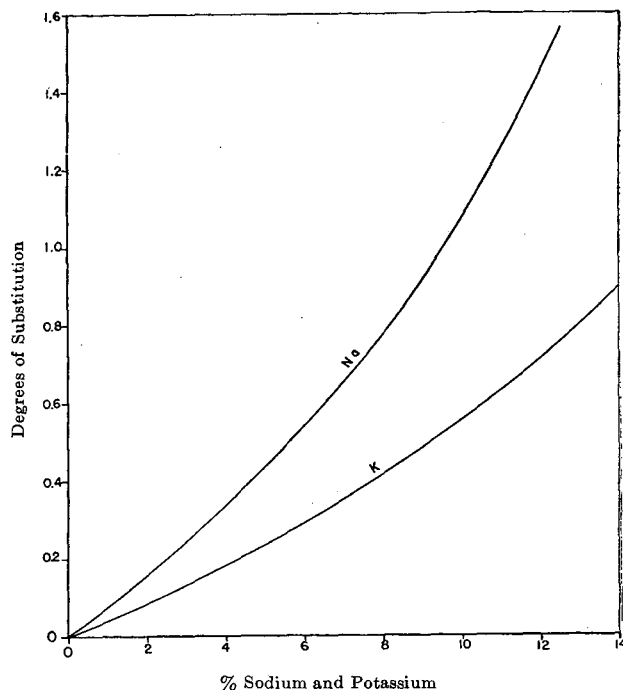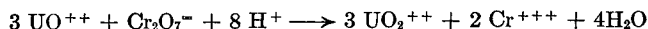
Figure 3. Degree of Substitution in Sodium and Potassium Carboxymethylcellulose

Table III shows the analysis of sodium and potassium in their respective salts of carboxymethylcellulose by the gravimetric and volumetric methods. The degree of substitution of the two salts of carboxymethylcellulose is shown in Figure 3. It can also be determined by a colorimetric method similar to the one described by Eyler, Klug, and Diephuis (5).

Table IV gives the analysis of aluminum carboxymethylcellulose by the two methods. The colorimetric method is the recommended procedure, as it is more rapid and can be carried out with greater ease and precision than the gravimetric 8-hydroxyquinoline procedure. The per cent sodium illustrates the useful-

ness of the magnesium uranyl acetate method for the determination of this common element and is of value in showing how the glycolate radical is distributed in the aluminum salt. The per cent glycolic acid was determined by a modified colorimetric method as described by Calkins (2).

Table IV. Analyses of Aluminum Carboxymethylcellulose Samples

| | Per Cent Aluminum | | | | Glycolic |
Sample	Colori-metric	8-Hydroxy-quinoline	Differ-ence	Sodium, %	Acid, %
A-1	3.18	3.17	0.31	0.23	17.2
A-2	3.28	3.27	0.30	0.15	20.0
A-3	3.28	3.17	3.35	0.19	15.0
A-4	3.64	3.58	1.65	1.76	16.1
A-5	4.95	4.84	2.23	2.98	30.0
A-6	5.20	5.09	2.11	2.15	31.0

Much work has been done pertaining to the use of Aluminon, ammonium aurintricarboxylate, in the colorimetric determination of aluminum. Composite aluminum reagents containing stabilizers such as gum arabic and gelatin have been used by Olsen, Gee, and McLendon (10) and Craft and Makepeace (4). Both reagents were investigated but were found to be time-consuming and the colorimetric curves produced by them were not suitable for the range of aluminum desired. The use of an aqueous solution of Aluminon as described by Sandell (11) proved to be the most suitable, as it was stable and easily prepared and gave the curve desired (Figure 4). The results obtained showed that the method was precise and that the determination was reproducible.

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Per Cent Aluminum
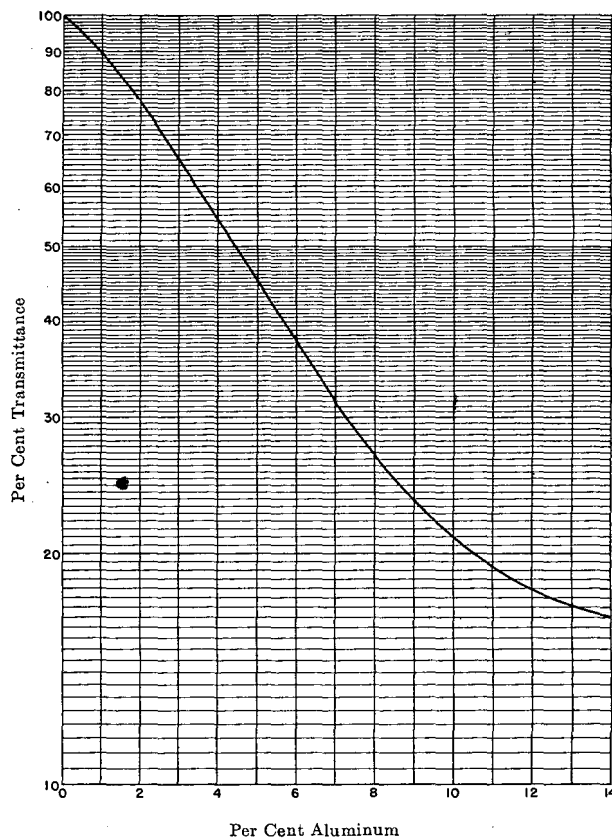
Figure 4. Determination of Aluminum

Cenco Type B-2 photelometer, with green filter 1.0% aluminum equals 0.01 mg.

Quantitative Determination of Dicyclopentadiene

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A method for the quantitative analysis of dicyclopentadiene consists of addition of formic acid to one of the double bonds and determination of the saponification equivalent of the resulting formate ester. The method is also applicable to the analysis of higher polymers of the hydrocarbon.

ALTHOUGH dicyclopentadiene and its monomer have become of considerable industrial importance in recent years, the few methods that have been developed for the quantitative determination of the dimeric hydrocarbon are subject to limitations. The method of Schultze (3), based upon bromination in the absence of oxygen, involves an elaborate procedure and is accurate to no more than about 2%. Uhrig, Lynch, and Becker (4) have described a method based upon the controlled depoly-

merization of dicyclopentadiene to the monomer, which is determined colorimetrically in the form of the phenylfulvene, but careful control is required because of the tendency of the monomer to polymerize at higher temperatures.

In a recent investigation of dicyclopentadiene the authors observed that one of the two double bonds of the hydrocarbon possesses an unusual power to add various reagents (1). Although Bruson (2) has stated that organic acids of dissociation constant higher than about 1.5×10^{-3} react with dicyclopentadiene in the absence of an electrophilic catalyst (sulfuric acid,

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boron trifluoride, etc.), the authors found that the hydrocarbon (I) reacts with formic acid ($k_a = 2.1 \times 10^{-4}$) at the reflux temperature to produce dicyclopentenyl formate (II) in very high yield.
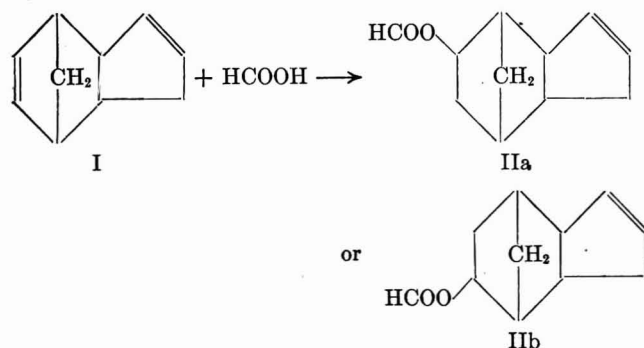
With a view to the development of an analytical procedure, a study has now been made of the factors governing the addition reaction and the subsequent saponification of the formate.

SAPONIFICATION OF DICYCLOPENTENYL FORMATE

When a mixture of dicylcopentenyl formate with 1.5 equivalents of 0.5 N ethanolic potassium hydroxide was allowed to stand at room temperature (22° C.), about 93% of the ester was saponified in the first half hour but a very long time was required for completion of the reaction. Further experiments were therefore conducted at the boiling point. The data reported in Table I were obtained by heating weighed samples of the formate with alcoholic alkali in a boiling water bath for varying periods of time, cooling the solutions, and immediately titrating the excess alkali. The results show that hydrolysis is 99.7 to 99.8% complete in 4 to 5 hours; a 6-hour period was decided upon as providing for completion of the reaction.

ADDITION OF FORMIC ACID TO DICYCLOPENTADIENE

Pure, crystalline dicyclopentadiene (melting point 32° C.) was used to study the optimum ratio of hydrocarbon to formic acid and the velocity of addition. When mixtures of the reactants in various molar proportions were refluxed for 8-hour periods, it was found that a quantitative conversion could be realized with

Table I. Saponification of Dicyclopentenyl Formate with 1.5 Equivalents of 0.5 N Potassium Hydroxide in Ethanol at Reflux Temperature

Time Min.	Yield by Titration %
5	92.7
10	92.9
20	93.3
30	93.7
60	94.8
90	95.7
120	96.6
150	97.5
180	99.2
240	99.7
300	99.8

Table II. Reaction of Dicyclopentadiene (1 Mole) with Formic Acid (3 Moles) at Boiling Point

(Analysis by saponification with 0.5 N ethanolic KOH for 6 hours)

Time of Reflux Hours	Ester %
1	93.1
2	95.4
3	98.1
4	99.5
5	99.9

Table III. Determination of Various Samples of Dicyclopentadiene

	Composition of Sample	Ester Found, %	Hydrocarbon Found, %
1	2.3207 grams of formate	99.8	..
2	2.4206 grams of formate + 1.8586 grams of pure dicyclopentadiene	99.7	..
3	3.0891 grams of formate + 2.0923 grams of technical dicyclopentadiene	99.65	..
4	2.672 grams of pure dicyclopentadiene + 3.272 grams of formic acid	...	99.9
5	2.3212 grams of technical dicyclopentadiene + 2.7821 grams of formic acid	...	91.8
6	2.1755 grams of technical dicyclopentadiene 0.6672 grams of pure dicyclopentadiene } + 2.8104 grams of formic acid	...	93.6 (calcd. 93.7)

2 moles of formic acid per mole of hydrocarbon, and a ratio of 1 to 3 was chosen for the further experiments recorded in Table II. The results show that a reflux period of 5 hours is satisfactory.

DETERMINATION OF DICYCLOPENTADIENE

Procedure. An accurately weighed sample of approximately 2.5 grams of dicyclopentadiene or a technical mixture containing the hydrocarbon is mixed with 2.5 grams of 99 to 100% formic acid in a flask with a ground-glass joint and the mixture is heated under reflux for 5 hours in an oil bath kept at 135° to 140° C. The flask is then removed and cooled, the condenser is rinsed with about 25 cc. of benzene, the solution is transferred to a separatory funnel, and the reaction vessel is rinsed with two 25-cc. portions of benzene. The organic layer is washed first with 15 cc. of distilled water and then with 15 cc. of saturated sodium bicarbonate solution to remove excess formic acid, and finally with two fresh portions of distilled water; separation of the layers proceeds very quickly. The benzene layer is returned to the reaction flask and an accurately measured volume (50.0 cc.) of 0.5 N potassium hydroxide in 95% ethanol is run in from a buret. The solution is refluxed for 6 hours and then cooled under the tap, the condenser is rinsed with 25 cc. of alcohol, and the excess alkali is titrated with 0.5 N hydrochloric acid, with phenolphthalein as indicator.

Calculation. % dicyclopentadiene = 6.6 ($a − b$)/weight of sample where a = cc. of acid required to neutralize 50.0 cc. of potassium hydroxide solution, and b = cc. of acid used to titrate sample.

The results reported in Table III indicate that the method is reliable to 0.5% or better and that impurities present in technical preparations of dicyclopentadiene do not interfere with the analysis. Since higher polymers of cyclopentadiene react with formic acid in the same manner as the dimer does (1), mixtures containing higher polymers must be separated prior to analysis by fractional distillation; in view of the large differences in the boiling points, such separation presents no difficulties. Orienting experiments with tricyclopentadiene indicated that interaction with formic acid and saponification of the formate proceed quantitatively also in this series.

Since cyclopentadiene dimerizes completely when kept at room temperature for a few days, the monomer may be determined by conversion to the dimer and application of the above procedure. A mixture of monomer and dimer can be analyzed by distilling off the monomer from one sample and determining the dimer in the residue, and simultaneously keeping a second sample at 20° to 25° C. for 4 to 5 days and determining the amount of total dimer.

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Removal of Metals at the Mercury Cathode

Separation of Interfering Metals in the Determination of Aluminum, Alkaline Earth, and Alkali Metals

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Methods are described for the clean, efficient separation of large quantities of elements deposited at the mercury cathode from those which are not affected (aluminum, alkaline earths, alkali metals, etc.); these methods are based on the use of a previously described unitized mercury cathode apparatus (4) suitable for industrial analytical applications. Procedures are given for the removal of 0.5- to 5.0-gram quantities of easily removable metals such as iron, copper, zinc, nickel, and cobalt, and for the removal of somewhat smaller quantities of chromium, lead, tin, and molybdenum which are not deposited under ordinary conditions. Results are reported that demonstrate the satisfactory extent to which these metals are removed and indicate the optimum values of such factors as voltage, current, surface area of the mercury, distance between electrodes, and time of electrolysis.

ELECTROLYSIS at the mercury cathode has long been recognized as a convenient, clean separation of certain metals prior to the determination of those elements which are not deposited (3, 5). Inefficient design of cells has prevented a full use of this technique, however, especially where large amounts of metal must be eliminated. A convenient, unitized dual apparatus which employs a new type of self-contained cell has recently been described (4); this paper presents the results of studies in the efficient use of this apparatus. Optimum operating conditions have been determined in regard to voltage, current, electrolyte, agitation of interface, surface area of cathode, number of mercury changes, time of electrolysis, distance between electrodes, and size of sample used. A large number of synthetic samples have been analyzed to test the efficiency of removal of unwanted metals and the manipulative losses of elements for which analysis was required. The method has also been used in the preparation of a variety of service samples and has been found equally valuable when the final analysis has been carried out by polarographic, colorimetric, or chemical means.

Special techniques were found necessary for the removal of such elements as lead, tin, chromium, and molybdenum. Their efficient removal depended on the valence state of the metal or the electrolyte used in the electrolysis.

APPARATUS

The self-contained electrolysis cell and dual unitized apparatus previously described (4) were used throughout the investigation. Fume hoods, shown in place above the electrolysis beakers in Figure 1, were designed and used when hydrochloric acid was required for electrolysis. Minor changes were made in the construction of the cell in order to study various factors.

EXPERIMENTAL

Optimum Operating Conditions. Several factors were investigated in an effort to determine the optimum conditions for the most efficient removal of metals with the apparatus. The amount of the major constituent remaining after electrolysis was determined by various means. The following were determined colorimetrically using the indicated reagents: copper by diethyldithiocarbamate, iron by *o*-phenanthroline, cobalt by nitroso-R-salt, mercury and zinc by dithizone, nickel by dimethylglyoxime, chromium by diphenylcarbazide, and molybdenum by thiocyanate–tin chloride. Cobalt, lead, and cadmium were determined by direct polarographic methods. Tin was weighed as the oxide.

CURRENT REQUIRED. Samples containing electrolytic copper were dissolved in nitric acid, evaporated to remove nitric acid, taken up in sulfuric acid, and electrolyzed for a constant time of 30 minutes with varying current, using a mercury surface area of 10.4 sq. cm. The voltage was held near 5 volts and the current was varied from 1 to 5 amperes by control of the electrolyte added. As shown in Table I, the amount of copper remaining in solution after electrolysis was approximately inversely proportional to the current used.

DISTANCE BETWEEN ELECTRODES. The optimum distance between the anode and the mercury pool was determined by using an electrode with an adjustable anode. A series of experiments was carried out, varying the distance between the electrodes from 3 to 20 mm. and maintaining the following electrolysis conditions: 500 mg. of iron; 10.4 sq. cm. of mercury area; electrolysis for 30 minutes at 5 amperes and approximately 5 volts. As shown in Figure 2, the optimum distance was found to be 8 to 10 mm. between the anode and cathode surfaces. When the electrodes were less than 4 mm. apart, a gas-block caused poor conduction and the amount of iron remaining in solution was greater than at distances of 8 to 10 mm.

AREA OF MERCURY CATHODE. The relation of surface area of the mercury to completeness of removal of a metal at the mercury cathode was studied by making cups of different diameters for the mercury and electrolyzing solutions containing
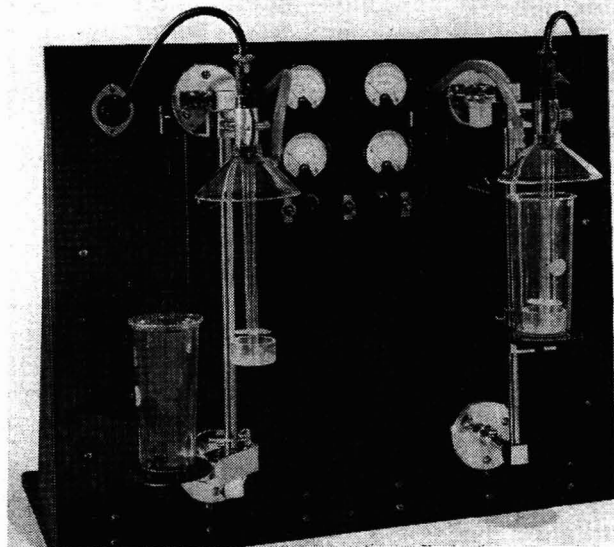
Figure 1. Dual Unitized Mercury Cathode Apparatus with Built-In Fume Hoods

Table I. Relation of Current Used to Completeness of Removal of Metal at Mercury Cathode

Copper Added	Electrolysis for 30 Minutes		Copper Remaining in Solution
Mg.	Amperes	Volts	Mg.
500	5	5	0.25
	3	5	0.54
	2	4	4.20
	1	5	16.00
250	5	5	0.06
	3	5	0.46
	2	4	0.90

Table II. Relation of Surface Area of Mercury to Completeness of Removal of Metal at Mercury Cathode

(Electrolysis for 45 minutes at 5 amperes)

Iron Added	Volume of Mercury	Surface Area of Mercury	Iron Remaining in Solution
Mg.	Ml.	Sq. cm.	Mg.
300	10	10.4	2.24
300	10	18.6	0.68
300	15	37.4	0.03

300 mg. of iron for 45 minutes at 5 amperes and approximately 5 volts. As shown in Table II, the amount of iron remaining in the solution was found to be roughly inversely proportional to the area of the mercury surface.

Efficiency and Applicability. COMMON METALS. When the mercury cathode is used to prepare samples for the analysis of a minor constituent, the efficiency of the electrolysis operation is best judged by the accuracy of the subsequent analysis performed rather than by the degree of removal of interfering elements. The evaluation sometimes depends on the method used in the final determination—for example, when the mercury cathode is used to remove a large amount of cobalt from a small amount of sodium, it is not generally possible to determine the sodium in the electrolyzed solution by the polarographic method (10), even though the resulting cobalt concentration is very low. On the other hand, it is possible to analyze such solutions successfully by the flame photometer method (1). Fortunately this condition is an exception rather than a rule for most applications.

Several series of samples, containing 1 mg. of sodium and as much as 5.0 grams of metal, were electrolyzed according to the following procedure:

Concentrate the neutral or slightly acid solution to be electrolyzed to 25 to 30 ml. and transfer it to a 250-ml. tall-form electrolytic beaker. Clamp the electrode assembly in place, fill the cathode with mercury to within 1 or 2 mm. of the top, and raise the beaker around the electrode until the electrode almost touches the bottom of the beaker. Turn on the current and carefully add concentrated sulfuric acid until a current of 5 amperes is attained. Cover the beaker with a split notched watch glass, electrolyze for 15 or 30 minutes, and add water as necessary to maintain constant volume. With the current on, lower the beaker and immediately rinse the electrode with a stream of distilled water. Replace the amalgam with clean mercury, electrolyze for 15 or 30 minutes, and rinse; repeat this cycle one or more times.

The regular (10.4 sq. cm.) cell assembly was used because it functioned best with the 250-ml. tall-form beaker and small volume of solution found convenient. Reagent grade metallic iron, copper, zinc, and mercury, and c.p. salts of cobalt, cadmium, and nickel were used in preparing the solutions. The electrolyzed solutions were analyzed for sodium by the polarographic method (10), except those from the cobalt removal which were analyzed by the flame photometer method (1). In each case, a reagent blank for sodium was determined on a comparable amount of metal and appropriate corrections were made in the results. The exact conditions used and results obtained are summarized in Table III. This procedure effectively removes 1 gram or more of the metals tested, allowing the determination of 1 mg. of sodium with an accuracy of ±0.04 mg. (4%) or less.

Table III. Efficiency of Mercury Cathode in Removing Metals from Solution in Preparation for Sodium Analysis

Element	Added	Found	Electrolysis Interval	Sodium Found[b]
	Mg.	Mg.	Min.[a]	Mg.
Copper	500	0.074	30, 30, 30	0.99
	1000	0.054	30, 30, 30	1.02
	2000	0.082	30, 30, 30	1.02
	5000	0.353	15, 15, 30, 30	1.03
Iron	500	0.068	30, 30, 30	1.02
	1000	0.212	30, 30, 30	1.04
Cobalt[c]	500	0.170	30, 30, 30	1.02
	1000	0.860	30, 30, 30	1.00
	2000	1.81	30, 30, 30	0.85
Cadmium	500	0.25	30, 30, 30	0.98
	1000	0.30	30, 30, 30	0.98
	2000	0.80	30, 30, 30	0.99
Mercury	500	0.016	30, 30, 30	0.99
	1000	0.010	30, 30, 30	0.96
	2000	0.060	30, 30, 30	0.98
Nickel	500	0.016	30, 30, 30	0.99
	1000	0.025	15, 15, 30, 30	0.97
	2000	0.065	15, 15, 15, 30, 15	1.00
	3000	0.230	15, 15, 15, 15, 30	1.03
Zinc	500	0.004	30, 30, 30	0.99
	1000	0.006	30, 30, 30	1.00
	2000	0.009	30, 30, 30	1.00

[a] Regular (10.4 sq. cm.) electrode; 5 amperes.
[b] 1.00 mg. of sodium added in each case.
[c] Sodium results determined by flame photometer in this case; by polarograph in all others.

One of the chief difficulties found in the removal of large amounts of metal with the apparatus was the rapid formation of a gelatinous amalgam which swells to fill the space between the cathode and anode, eventually stopping the electrolysis. This difficulty was circumvented to some extent by replacing the mercury before it happened; sometimes four such changes were required (see Table III). Even under the latter conditions, no tendency toward low sodium results was found when precautions of washing the electrode were observed. The agitation of
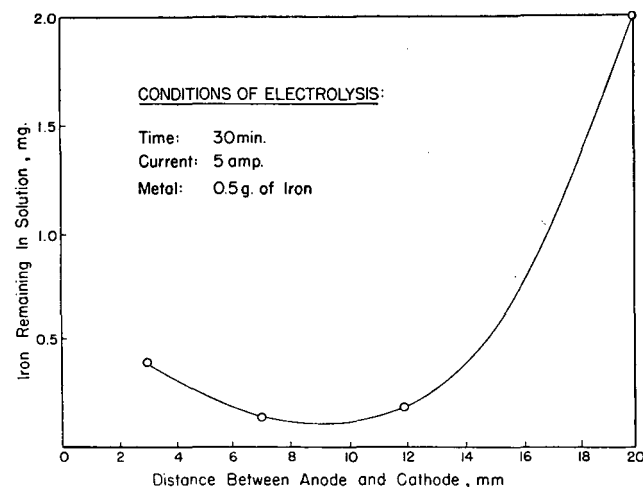
Figure 2. Effect of Distance between Electrodes on Completeness of Metal Removal at Mercury Cathode

the surface of the cathode by means of the iron-in-glass agitator (4) also aided in the deposition of large amounts of metal and prevented some of the tendency to short out by swelling. For efficient operation in general service work, the regular cell (10.4 sq. cm.) is recommended, using a sample size which is equivalent to 0.5 gram of metal. If a larger sample is necessary to determine trace amounts of a constituent, a larger cell is recommended using more mercury with greater surface area.

The mercury cathode procedure has been advantageously used for the removal of a variety of metals in the analysis for micro- and macroquantities of certain metals other than sodium. Aluminum was separated from a large excess of iron and determined colorimetrically; calcium was separated from iron, nickel, and chromium, and determined by a microtitration of calcium

Table IV. Analysis of Bureau of Standards Samples for Calcium and Aluminum after a Mercury Cathode Electrolysis

Sample	Calcium Oxide		Aluminum Oxide	
	N.B.S. value	Found	N.B.S. value	Found
		Per cent by weight		
Crescent iron ore, No. 26	2.64	2.44 2.46	1.02	1.04 1.07
Ferrosilicon, No. 58	0.63	0.64 0.64	1.44	1.36 1.29

oxalate with perchlorato cerate; a thorium sample was cleaned of interfering metals by electrolysis before determination of the thorium as the oxide. Calcium and aluminum results obtained in the analysis of two National Bureau of Standards samples after electrolysis at the mercury cathode are shown in Table IV. In general, any of the alkali, alkaline earth, or other metals not deposited at the mercury cathode can be separated by this means from those metals which are easily deposited in the mercury.

Metals Requiring Special Techniques. CHROMIUM. When samples containing chromium were electrolyzed, a precipitate of chromium black generally formed on the cathode surface, necessitating a filtration for removal of the chromium from the solution. Chirnside (2) studied the problem in detail but did not find a completely satisfactory solution. During the course of investigating the deposition of chromium, it was noticed that amalgamation took place satisfactorily when trivalent chromium salt was used as a starting material, but that the black precipitate was invariably formed when hexavalent chromium salt was used. Various methods were investigated for reducing chromium in samples to the trivalent state; reduction with hydrogen peroxide was found to be the most satisfactory, because the excess peroxide is easily decomposed by boiling prior to electrolysis. It was found that the amalgam formed by electrolyzing trivalent chromium solutions will eventually decompose and form a black precipitate in the cell when the current is not maintained. The procedure was highly efficient, giving solutions containing as little as 6 micrograms of chromium (4).

TIN. Insoluble tin salts precipitated and prevented deposition of tin at the cathode when the regular procedure using sulfuric acid was employed. Schoch and Brown (9) plated out tin and the metals of the tin group on a copper-plated platinum electrode by using hydrochloric acid as an electrolyte and by having hydroxylamine hydrochloride or oxalic acid present during the electrolysis. It also appeared from their work that good deposition could not be expected unless a low current (2.5 amperes) were used. After a preliminary study of the various factors, the following procedure was evolved and successfully applied to the separation of tin from sodium. The results obtained under various conditions are given in Table V. While the tin was reduced only to 3 or 4 mg., the removal was adequate to prevent interference in the determinations of 1 mg. of sodium.

Table V. Efficiency of Tin Removal by Mercury Cathode from Hydrochloric Acid Solutions Containing Hydroxylamine

(Cell potential approximately 2 volts; regular 10.4 sq. cm. electrode)

Tin, Mg.		Electrolysis		Sodium, Mg.	
Added	Found	Current, amp.	Interval, min.	Added	Found
500	200	5	90	0.0	Nil
250	12.4	2.5	30, 15, 10	0.0	Nil
250	9.8	2.5	30, 15, 10	0.0	Nil
250	4.3	2.5	30, 30, 30	1.0	0.97
250	3.4	2.5	30, 30, 30	1.0	0.98

Procedure. Dissolve the sample in 20 ml. of concentrated hydrochloric acid and add 2 grams of hydroxylamine hydrochloride. Adjust the solution to a volume of 50 ml., cover the beaker with a fume hood, and electrolyze the solution at 2.5 amperes or less for 30 minutes. With the current on, lower the beaker and

immediately rinse the electrode with a stream of distilled water. Replace the amalgam with clean mercury, electrolyze for 30 minutes, and rinse; replace the mercury and repeat the cycle again.

LEAD. The formation of lead peroxides on the anode shorted the cell and prevented successful deposition of lead at the mercury cathode when the usual sulfuric acid medium was used. A modification suggested by Sand (7) for deposition of lead on a platinum cathode was found to be the basis of a satisfactory procedure for the mercury cathode. A procedure was evolved similar to that for tin in which the electrolysis is conducted in a solution of hydroxylamine in hydrochloric acid; using 2.0 grams of hydroxylamine and 0.3 N hydrochloric acid, the deposition of the lead proceeded smoothly at approximately 5 volts and 5 amperes. As shown in Table VI, this procedure gave sufficient deposition of lead for satisfactory recovery of 1 mg. of sodium by the polarographic method.

Table VI. Efficiency of Lead Removal by Mercury Cathode from Hydrochloric Acid Solutions Containing Hydroxylamine

[Electrolysis for three 30-minute periods at 5 volts and 5 amperes using regular (10.4 sq. cm.) electrode]

Lead, Mg.		Sodium, Mg.	
Added	Found	Added	Found
500	9.0	0.0	Nil
500	11.0	0.0	Nil
500	2.8	1.0	0.99
500	4.7	1.0	1.02

Table VII. Efficiency of Molybdenum Removal by Mercury Cathode from Sulfuric Acid Solution

[Electrolysis for two 45-minute periods at 5 volts and 5 amperes using regular (10.4 sq. cm.) electrode]

Molybdenum, Mg.		Sulfuric Acid Normality	Sodium, Mg.	
Added	Found		Added	Found
100	0.82	1.25	0.0	Nil
100	0.41	1.25	1.00	1.02
100	0.56	1.25	1.00	0.96

MOLYBDENUM. When attempts were made to electrolyze solutions of molybdenum by the standard mercury cathode procedure, the clear solution turned deep blue, and became very dark and gelatinous as the electrolysis proceeded. The use of hydroxylamine in hydrochloric acid solution had no effect on the deposition of molybdenum, but the use of a 1.2 N sulfuric acid solution enabled the electrolysis to proceed at the mercury cathode, as had previously been found by Merrill and Russell when using platinum (6). Samples containing 0.1 gram of molybdenum were electrolyzed for a total of 90 minutes with two mercury changes at approximately 5 volts and 5 amperes. As shown in Table VII, this procedure reduced the molybdenum content to less than 1 mg. (Some difficulty was found in the polarographic determination of sodium after the molybdenum deposition, for a reduction wave was superimposed on the crest of the sodium wave; this difficulty was eliminated by the use of 1 N tetraethylammonium hydroxide instead of the usual 0.1 N, but the cause of the difficulty was not determined.)

BISMUTH, ANTIMONY, AND ARSENIC. Deposition of bismuth, antimony, and arsenic has been reported by others, presumably when using a low, controlled potential (8). No success was found when large amounts (more than 100 mg.) were electrolyzed under the various conditions possible with the apparatus used; small amounts of these metals were not tested.

SUMMARY

The dual, unitized mercury cathode electrolysis unit with a self-contained cell has been demonstrated to be a practical method of removing a large number of metals from solution in the preparation of samples for analysis of those elements not removed during the electrolysis (such as aluminum, calcium, and sodium).

One-half gram of these metals can be removed easily in 90 minutes; larger amounts can be removed by changing the mercury more frequently or by using a larger cathode with more surface area. Small amounts of aluminum, alkaline earth, and alkali metals have been determined after the removal of large amounts of various metals. While the work reported in this paper emphasizes the preparation of samples for the determination of a minor constituent, the same techniques are expected to be useful in the determination of a major constituent. Procedures are given for the removal of considerable amounts of tin, lead, chromium, and molybdenum in a short time.

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Capillary-Tube Viscometer

For Routine Measurements of Dilute High-Polymer Solutions

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A capillary-tube viscometer is described which is particularly suited for the routine measurements of dilute high-polymer solutions. Its design minimizes the time required for the measurement, including the necessary operations of filling, cleaning, and drying the viscometer. Consideration is given to errors, including those produced when the differences in densities and velocities of flow (kinetic-energy correction) of the solvent and the solution are neglected.

THE growing interest in high polymers has produced a considerable increase in the number of viscosity determinations of dilute polymer solutions as a convenient method of characterizing their molecular weight. This, in addition to the frequent necessity of measuring viscosities at two or more dilutions in order to obtain the infinite dilution value, has made the reduction of the time required for a single measurement almost imperative, so as to minimize the effort expended in comprehensive surveys.

In so far as the operational efficiency of the conventional U-tube (Ostwald) viscometer is concerned, the principal disadvantages are: the time-consuming nature of the filling, rinsing, and drying operations, and the use of a fixed quantity of liquid, which produces a wide range of outflow times, depending upon the viscosity of the solvent or solution. Moreover, the design is, for reasons of compactness, usually such as to produce an appreciable kinetic energy contribution, which, if neglected, induces an appreciable error in the desired results.

This paper describes a capillary viscometer which either avoids or minimizes these disadvantages, although it may require as much as 60 cc. of liquid for its operation. A single determination of outflow time, including filling, level adjustment, cleaning, and drying operations, can be completed in from 3 to 6 minutes, in most cases, irrespective of the viscosity of the solvent employed.

VISCOMETER

The viscometer is essentially a modification of the form originally described by Scarpa (1, 5). The front and side views of the complete apparatus are shown in Figure 1, including the viscometer, A; the thermometer, and thermometer jacket, B; and provision for fluorescent illumination in box C, behind ground glass D.

The viscometer itself, shown in detail in Figure 2, consists of an inner and an outer assembly, the latter a water-jacketed tube, E, whose internal diameter is 20 mm. The uppermost end of this tube carries a 14/35 standard-taper joint, F, and a vent tube, G; the lower end, a stopcock, H. The jacket should extend over as long a portion of the tube as possible, and the tubing used in the fabrication of this part of the viscometer should be free of striae and surface irregularities. Such tubing, as well as precision-bore capillary, can be obtained from the Fischer-Porter Co., Hatboro, Pa.

The inner assembly or tube consists of a measuring bulb, J, and the capillary, M. The bulb should have a volume of about 1 cc. as defined by the transit marks, K and L. The interior surfaces of the bulb should be as nearly vertical as possible in order to minimize errors due to drainage. The transit marks are engraved on 8-mm. sections of 2-mm. bore tubing. The capillary, M, is precision-bore tubing of about 0.5-mm. bore and 190 mm. in length.

Beginning at a point about 3 cm. below the lower transit mark, the capillary is engraved at sixteen regularly spaced intervals of 1 cm. along its length. By means of these marks, called filling marks, the average liquid head in the viscometer may be easily adjusted to any one of sixteen values.

A cap, P, is provided to keep dust out of the instrument and, as described below, as an adjunct in the drying operations. The joint, F, should be snugly fitted; its registration marks, shown in Figure 2, should not be permanently affixed until the optimum position of coaxiality of the inner and outer assemblies has been established. These marks ensure reproducibility of capillary verticality.

Thermostated water is circulated through the thermometer and viscometer jackets by a suitable pump. The temperature, as read on the thermometer of the apparatus, should be within 0.1° of the desired value.

The stopcock should be lubricated with a small amount of a good-quality grease, except when the viscometer is to be used in the measurement of water or of aqueous solutions, in which case graphite, such as may be obtained from an ordinary pencil, should be used. Although most stopcock greases are more or less soluble in organic liquids, tests indicate that the amount dissolved from the stopcock barrel over a period of 15 hours was insufficient to produce any detectable increase in the efflux time.

Front Elevation   Side Elevation
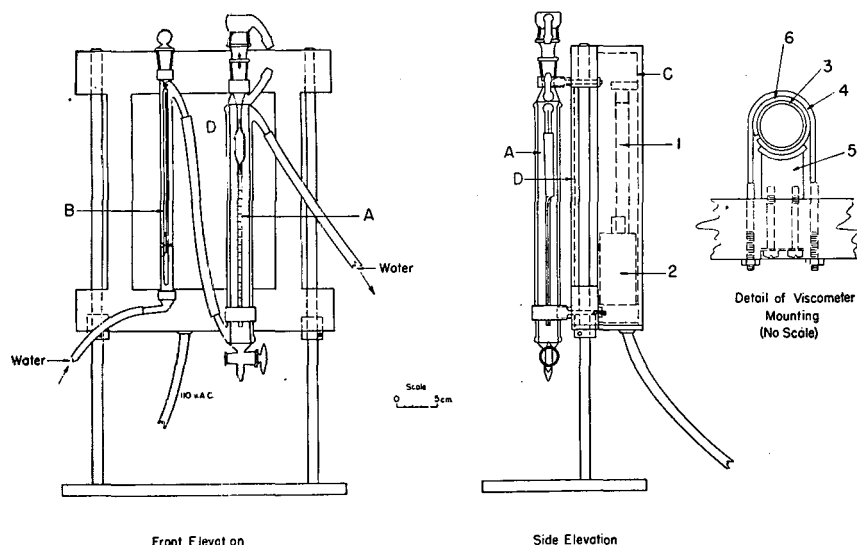
Figure 1. Complete Viscometer Assembly Including Detail of Mounting

A. Viscometer
B. Thermometer and thermometer jacket
C. Wooden box
D. Ground-glass plate
1. Fluorescent tube (2)
2. Transformer (2)
3. Glass wall of viscometer
4. Brass strap, $^1/_{16}$ inch thick
5. Brass block with section of piece of brass tube soldered on
6. Cushion of elastic polymer

No lubricant need be used on joints F and P.

Method of Operation. A quantity of liquid sufficient to bring the level above the desired filling mark is poured into the jacketed tube. The temperature of this liquid should be approximately that of the measurement, in order to expedite the speed of attaining thermal equilibrium. After the inner assembly has been aligned and seated, the liquid level is adjusted to the desired filling mark, followed by a final adjustment after a short interval to allow the completion of thermal equilibrium and drainage. A reasonable amount of care is required in the level adjustment, since the efflux time is relatively sensitive to errors in the average internal head.

The measuring bulb is then filled by the application of pressure at G, and the time required for the volume of liquid contained between the transit marks to flow out is obtained in the conventional way. A manually operated stopwatch, accurate to 0.2 second, is sufficient for this purpose.

Upon completion of the measurement of outflow time, the liquid is drawn off through the stopcock, using suction through a suitable trap. The interior surfaces of the viscometer are then rinsed with a polymer solvent, preferably, one which is also relatively volatile (not necessarily the solvent employed in the solution). If such a rinse liquid cannot readily be found, the rinsing operation should be carried out using two liquids consecutively, the first a polymer solvent and the second a volatile liquid.

The following very simple rinsing procedure, consisting of three basic operations, has been found adequate: Rinse out the measuring bulb and the capillary by drawing two or three 1-cc. portions of solvent through them by applying suction at the stopcock and closing tube G. Using a wash bottle, rinse the outside surface of the inner assembly while slowly withdrawing it. Wash the interior walls of the outer assembly, using the inner assembly as a guide in directing the liquid to all interior surfaces.

The instrument is reassembled and the side arm of the cap, carrying a short piece of flexible tubing, connected to the vent tube. The moderate suction, applied during the rinsing process, is increased to the maximum obtainable by a water aspirator, thereby quickly evaporating any liquid remaining in the instrument.

In the measurement of water and aqueous polymer solutions, the following conditions should be observed: (1) All grease (lubricant) should be removed from the stopcock and the instrument thoroughly degreased; a thin layer of graphite, such as may be obtained from an ordinary lead pencil, may be used as a lubricant in the stopcock. (2) On filling the viscometer, care

must be exercised to avoid foam, which interferes with the accurate adjustment of liquid level. This may be done either by very carefully flowing the liquid down the wall, or by sucking it into the instrument through the drain-off tip, using a suitable extension. (In the latter process the inner assembly must be removed.) (3) Organic liquids must not be used in the drying operation, as they are almost certain to introduce grease into the instrument. It is recommended that drying either be accomplished by evaporating the rinse water remaining or else be entirely avoided by displacing the "retiring" liquid with the next liquid to be measured. The displacement method is more rapid, although its use will require somewhat more than the usual quantity of liquid—e.g., 100 cc.

The viscometer is designed to be used at or near room temperature for the most efficient operation. Satisfactory results have been obtained at jacket temperatures as high as 40° C., but such use is not recommended as a routine practice, owing to the additional time which must be allowed for the upper parts of the inner assembly (in the gaseous space above the liquid) to come to temperature. If the instrument must be employed occasionally at high temperatures, the inner parts may be brought to temperature somewhat more quickly by filling and emptying with liquid prior to the adjustment of liquid level and the measurement of outflow time.

PERFORMANCE OF VISCOMETER

Range of Solvent Outflow Time. It is apparent from the foregoing discussion that the provision of multiple filling levels enables the operator readily to adjust the outflow time of various solvents of different viscosity, so that they are neither inefficiently long nor inaccurately short. The relation between the filling-mark number and the solvent outflow time is shown in Figure 3 for five representative materials. The figures along the curves denote the minimum polymer concentration that can be measured at the indicated level without producing an error in the inherent viscosity $(2, 6)$, $\Delta\{\eta\}$, greater than 0.01 unit. (These values are based on an uncertainty of 0.2 second in the determination of the outflow times of the solvent and of the solution.)

The existence of a minimum concentration, C_m, below which
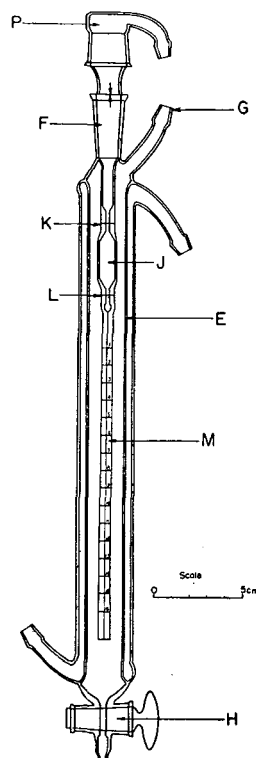
Figure 2. Viscometer

Table I. Dependence of $f(\eta_r)$ on Relative Viscosity, η_r

η_r	$f(\eta_r)$
1.000	1.414
1.250	1.280
1.500	1.200
2.000	1.118
4.000	1.031
10.000	1.005
∞	1.0000

one cannot measure depends upon the values of t_0, Δt, η_r, and $\Delta\{\eta\}$, and is given by the relation:

$$C_m = \frac{\sqrt{(\eta_r.\Delta t)^2 + (\Delta t)^2}}{\eta_r.t_0.\Delta\{\eta\}} = f(\eta_r)\ \frac{\Delta t}{t_0\Delta\{\eta\}} \qquad (1)$$

Equation 1 is derived by combining the error equation, $\eta_r = \sqrt{(\eta_1\Delta t)^2 + (\Delta t)^2}/t_0$, of the approximation, $\eta_r \approx t/t_0$, with Equation 6 of the following paper (6). The form of Equation 1 is such that the magnitude of $f(\eta_r)$, hence also of C_m, depends only to a very slight extent on η_r. This is shown in Table I.

In the use of Equation 1 as a guide it is expedient, in general, to set $f(\eta_r)$ equal to 1.2, from which it follows that C_m is virtually independent of the polymer molecular weight. If inherent viscosity determinations, precise to ±0.01, are to be made for concentrations less than those indicated in Figure 3, it is necessary either to employ conditions yielding sufficiently large values of t_0 or to increase the precision of timing. The latter may be accomplished by adapting automatic devices, such as those described by Jones and Talley (3) and by Riley and Seymour (4).

When the outflow times of commonly used solvents have been established at the various levels, it is necessary to redetermine them only occasionally as a check on the cleanness of the capillary, or when changes associated with batch differences are likely to have occurred.

In the measurement of acetone solutions, for example, it will be noted that the optimum level corresponds to marks 1, 5, 11, and 16 for solutions containing 0.25, 0.50, 0.75, and 1.00 gram per 100 cc., respectively. If the 0.50% solution were to be evaluated by adjusting the level to a mark higher in number than 5, then a timing error of 0.2 second alone would produce an error in the inherent viscosity of greater than 0.01; whereas an adjustment of level to a number less than 5 would have the disadvantage of increasing the total time required for the measurement.

Throughout this and the following paper (6) the precision measure has been expressed on an absolute rather than a percentage basis. This is done for two reasons: (1) A constant absolute error, provided it is sufficiently small, is at least as satisfactory to the polymer technologist as a fixed percentage error; and (2) the absolute error permits a far greater latitude in instrument dimensions, timing error, etc., over the entire probable range of measurements than would be possible on a percentage basis. This becomes apparent when one considers that, on a constant percentage basis, an error, the magnitude of which would be acceptable at high inherent viscosities, would require such a small absolute error at low viscosities that it would necessitate far more precise measurements than the use of the data usually warrants.

The choice of an error of ±0.01 is admittedly somewhat arbitrary. From the authors' experience it seems improbable that greater precision than this will be generally required for routine measurements. In certain cases it is conceivable that even less precise data might suffice; if an allowable tolerance of ±0.05 is permissible, most, if not all, of the discussion of this and the following section may be disregarded.

Range of Applicability of the Approximation: $\eta_r \approx t/t_0$. In the preceding discussion it is assumed that the relative viscosity is

adequately expressed by the ratio of the outflow times, t/t_0, of the solution and the solvent. In making this approximation, two factors, the contribution of the density ratio of the corresponding liquids and the contribution of the kinetic-energy correction, are assumed to be negligible. The importance and magnitude of these factors have been discussed elsewhere (6). In this discussion it was shown that the density factor is completely independent of the viscometer dimensions, and depends entirely upon the solute-solvent system. In general, it is improbable that this factor will ever amount to more than ±0.01 unit, and may be considerably less.

The density contribution to the inherent viscosity, $\Delta\{\eta\}_{dens.}$, may be calculated from the equation:

$$\Delta\{\eta\}_{dens.} = \frac{1}{d_0} \times \frac{\Delta d}{\Delta C} \qquad (2)$$

where d_0 is the density of the solvent and $\Delta d/\Delta C$ is the increase (or decrease) of the solution density with the polymer concentration.
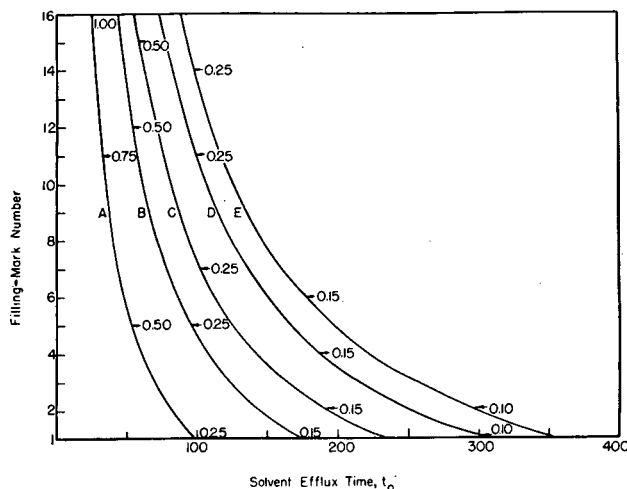
Figure 3. Relation between Filling-Mark Number and Solvent Efflux Time for Five Liquids

A. Acetone
B. Benzene
C. Water
D. Dioxane
E. Ethanol (absolute)

Values along curves show the concentrations (in grams per 100 cc.) of polymer solutions for which the indicated efflux times and filling-mark number are minimal. Units of t_0 are in seconds.

The contribution of the kinetic-energy factor to the inherent viscosity, denoted by the symbol: $\Delta\{\eta\}_{k.e.}$, is always positive. Its magnitude is given, for any viscometer, by the following expression:

$$\Delta\{\eta\}_{k.e.} = \frac{V}{8\ \pi l} \times \frac{1}{\nu_0 t_0} \times \left(\frac{\alpha^2 - 1}{\alpha^2}\right)\bigg/ C \qquad (3)$$

where ν_0 is the kinematic viscosity of the solvent ($= \eta_0/d_0$), and α is the efflux time ratio, t/t_0. In Figure 4 this equation is represented nomographically. Although this nomograph is applicable only to the viscometer described in this paper, for which $V/8\pi l = 0.00243$, the construction is such that its applicability can be made completely general by reconstructing the t_0-scale.

The method of using the nomograph is as follows:

The value of the kinematic viscosity of the solvent (Scale 1) is aligned with the solvent efflux time (Scale 3) to determine the appropriate value of K on Scale 2. The K-value obtained is then

$\eta_0 \times 10^2$ t_0 $K \cdot f(\alpha)$ $\Delta\{\eta\}_{k.e.}$
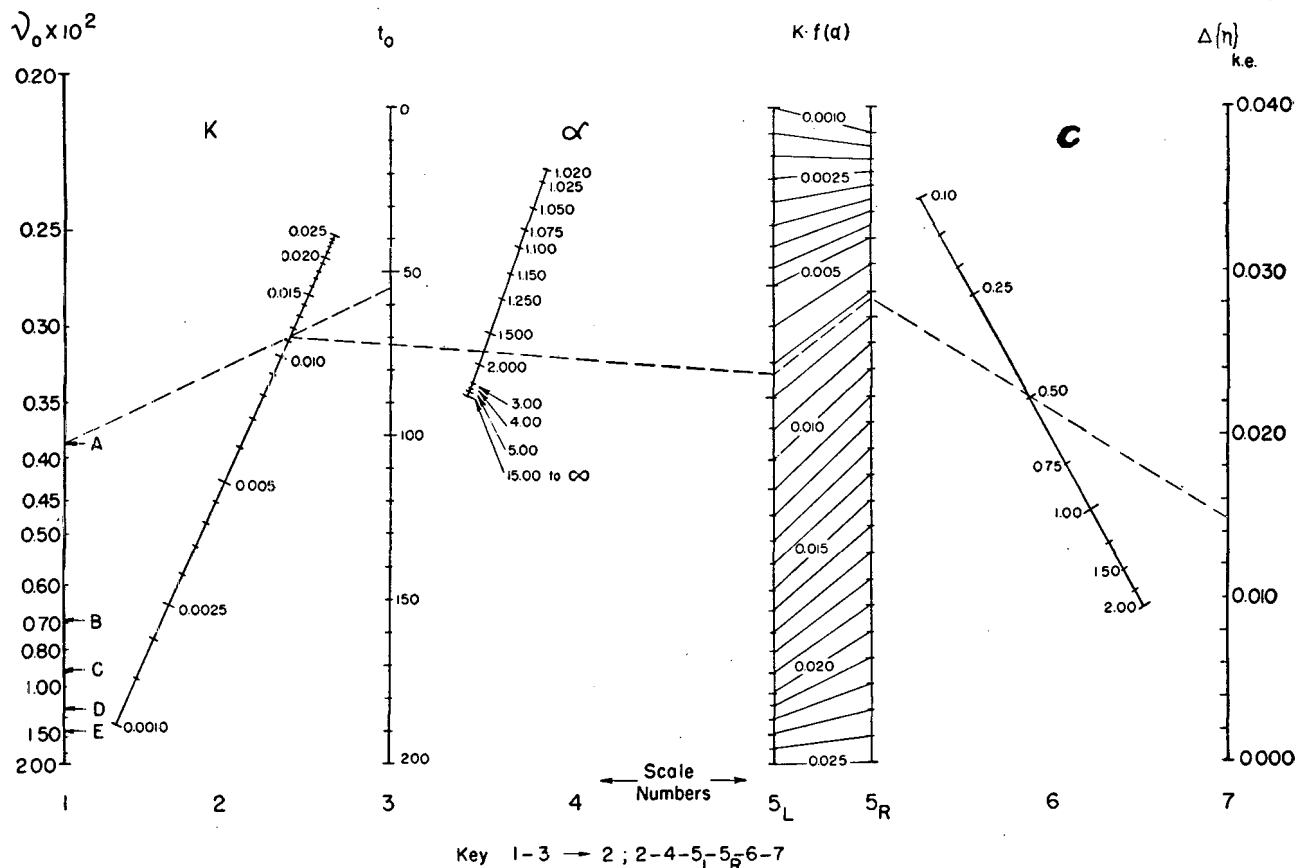
Figure 4. Nomograph for Calculating Kinetic-Energy Contribution to Inherent Viscosity

Table II. Magnitude of Kinetic-Energy Factor for Acetone Solutions at 25° C.

Inherent Viscosity	$\Delta\{\eta\}_{k.e.}$ for:				
	$C = 0.25$ $t_0 = 100.0$	$C = 0.50$ $t_0 = 55.0$	$C = 0.75$ $t_0 = 3.50$	$C = 1.00$ $t_0 = 25.5$	$t_0 = 100.0$
0.10	0.0012	0.0025	0.004	0.005	0.0011
0.50	0.0056	0.010	0.013	0.015	0.004
1.00	0.010	0.015	0.019	0.020	0.005
2.00	0.015	0.020	0.023	0.025	0.006
3.00	0.018	0.021	0.023	0.025	0.006
4.00	0.022	0.023	0.024	0.025	0.006

Note effect of using longer time of outflow (for $C = 1.00$ gram per 100 cc.) on $\Delta\{\eta\}_{k.e.}$

aligned with the efflux time ratio, α, to determine a point on Scale 5_L. After normalization (Scale 5_L to 5_R), this point, when combined with the concentration of the solution, yields the desired result, $\Delta\{\eta\}_{k.e.}$, on Scale 7.

The maximum possible value of $\Delta\{\eta\}_{k.e.}$ will be 0.025 for acetone, 0.013 for benzene, 0.009 for water, 0.007 for dioxane, and 0.005 for ethanol solutions at 25° C. Table II is illustrative of the magnitude of this factor for typical conditions for which it is of the greatest importance.

TREATMENT OF EXPERIMENTAL DATA

When the outflow times of several dilutions of a polymer solution are obtained, the ratio of each to their corresponding solvent outflow times is calculated. These quantities, t, t_0, and α, are shown for a typical case in columns 3, 4, and 5 of Table III, which is in the form of a report sheet. The approximate inherent viscosity, $\ln \alpha/C$, is then calculated for each solution (column 6). These values, as determined with the instrument described, will be within 0.02 or 0.03 unit of the fully corrected inherent viscosity. If more accurate results are required, the correctional terms $\Delta\{\eta\}_{dens.}$ and $\Delta\{\eta\}_{k.e.}$, must be evaluated (Equations 2 and 3, or by Figure 4) and added to the approximate inherent

Table III. Polymer Viscosity Report

Date 9/24/46
Observer C. L. T.

A. Description of Polymer. Cellulose acetate, 40% acetyl, No. 133475
B. Description of Solvent. Acetone, Batch No. C460-55

Absolute Viscosity. 0.0030 poise
Density, d_0. 0.784 gram per cc. } at 25 ° C.
Kinematic Viscosity. 0.0038 stoke

C. Temperature of the Determination. 25 ° C.
D. Data on Solutions. The density, d_c, of a solution for which $C = 1.00$ gram per 100 cc., is 0.789 gram per cc.

Concentration, G./100 Cc.	Filling-Mark No.	Efflux Time Soln. t	Solvent t_0	α ($= t/t_0$)	$\dfrac{\ln\alpha}{C}$	$\Delta\{\eta\}_d$	$\Delta\{\eta\}_{k.e.}$	$\{\eta\}$
0.250	1	160.8	99.7	1.613	1.91	0.006	0.015	1.93
0.400	4	130.4	62.0	2.104	1.86	0.006	0.019	1.88
0.600	7	131.0	45.0	2.910	1.78	0.006	0.021	1.81
0.800	11	131.7	33.8	3.896	1.70	0.006	0.022	1.73

E. Results. Intrinsic Viscosity 2.00
F. Remarks. Intrinsic viscosity was obtained by extrapolation of $\{\eta\}$-values to infinite dilution.

viscosity. The fully corrected viscosity will then be accurate to ±0.01 unit.

The infinite dilution value, the intrinsic viscosity, is obtained by graphical methods from either the approximate or fully corrected inherent viscosities, depending upon the accuracy required. The intrinsic viscosity will be of the same order of accuracy as the inherent viscosities from which it was obtained.

After a considerable amount of data has been obtained for any solute-solvent system over a wide range of polymer molecular weight, it is possible to derive a simple quantitative relation between the intrinsic and the inherent viscosity, the latter being evaluated at a constant, fixed concentration—e.g., 0.25 gram per 100 cc. (7). When this has been done, a single determination of

efflux time of the solution will suffice to determine the intrinsic viscosity of the polymer.

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Application of Corrections in Viscometry of High-Polymer Solutions

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The importance of the relative densities and of the so-called kinetic-energy correction in the measurement of the relative viscosities of polymer solutions is discussed. Equations are derived relating the separate and combined contribution of these factors to the relative viscosity and to the inherent viscosity, an important polymer-characterizing function. A nomograph is presented by means of which the kinetic-energy correction contribution may be easily and quickly evaluated.

IN THE measurement of the relative viscosities of dilute high-polymer solutions by the capillary-tube method, it is often assumed that the simple ratio of the efflux times of the solution and the solvent is an adequate quantitative expression of the relative viscosity and of quantities derived therefrom—e.g., the specific viscosity, inherent viscosity, etc. This procedure may produce significant inaccuracies.

This was recognized by Schulz (3) in his treatment of some of the errors incident to the application of the capillary viscometer in the measurement or evaluation of the specific viscosities of polymer solutions. In his analysis of the error produced by neglecting the so-called kinetic-energy term it is justifiably assumed that the densities of the solution and the solvent may be considered equal. The direct consequence of neglecting the density factor was not dealt with, probably because it is not dependent upon the dimensions of the viscometer. His treatment and results of the kinetic-energy error which are presented in a form not easily or immediately useful to the technologist, are less general both in form and in application than are given in this paper. The following argument, developed by a different approach and, unfortunately without prior knowledge of Schulz's contribution, yields a result which is in quantitative agreement with his findings.

It is well known that the difference between the relative viscosity, η_r, and the simple ratio of the efflux times, t/t_0, depends upon (1) the ratio of the corresponding densities, d/d_0; and (2) the kinetic-energy (capillary-end) correction, which is given by the last term of Equation 1. The complete expression for the relative viscosity may be written as:

$$\eta_r = \frac{d\,t}{d_0 t_0} + \frac{mVd}{8\pi l\,\eta_0 t}\left[(t/t_0)^2 - 1\right] \qquad (1)$$

where V is the volume of the "measuring bulb" in a conventional capillary viscometer, l is the length of the capillary, and m is a dimensionless coefficient, the kinetic-energy coefficient, which

we shall assume to be unity. The coefficient of absolute viscosity of the solvent is represented by η_0, and d and t are the density and the efflux time, respectively, of the solution. The corresponding quantities for the solvent are denoted by the subscript. In the following discussion it is convenient to set $d/d_0 = \beta$, $t/t_0 = \alpha$, and $Vd_0/8\pi l\eta_0 t_0 = K$, so that Equation 1 becomes:

$$\eta_r = \alpha\beta + \beta K \times \frac{\alpha^2 - 1}{\alpha} \qquad (2)$$

The use of the term "inherent viscosity" to represent the value of the quantity, $\ln \eta_r/C$, at finite values of C follows the suggestion of Cragg (1). It will be denoted by the symbol $\{\eta\}$. This function should be carefully distinguished from the intrinsic viscosity, $[\eta]$, which is the infinite dilution value of the inherent viscosity:

$$\{\eta\} \equiv \ln \eta_r/C = f(C)$$
$$[\eta] \equiv \lim_{C \to 0} \{\eta\} \neq f(C) \qquad (3)$$

the concentration being expressed in units of grams per 100 cc.

CONTRIBUTION OF THE DENSITY FACTOR

To the Relative Viscosity. The contribution of the density factor, β, to the relative viscosity is given by the equation:

$$(\Delta\eta_r)_{\text{dens.}} = \frac{\partial\eta_r}{\partial\beta'} \times \Delta\beta = \alpha\Delta\beta + K \times \frac{\alpha^2 - 1}{\alpha} \times \Delta\beta \qquad (4)$$

where $\Delta\beta$ is the amount by which the density ratio, β, differs from unity. Since, in most cases, the quantity, $K(\alpha^2 - 1)/\alpha$, is small compared with α, Equation 4 reduces to:

$$(\Delta\eta_r)_{\text{dens.}} \approx \alpha\Delta\beta \qquad (5)$$

This approximation is admissible, inasmuch as the error produced in making it is of second-order magnitude. A similar
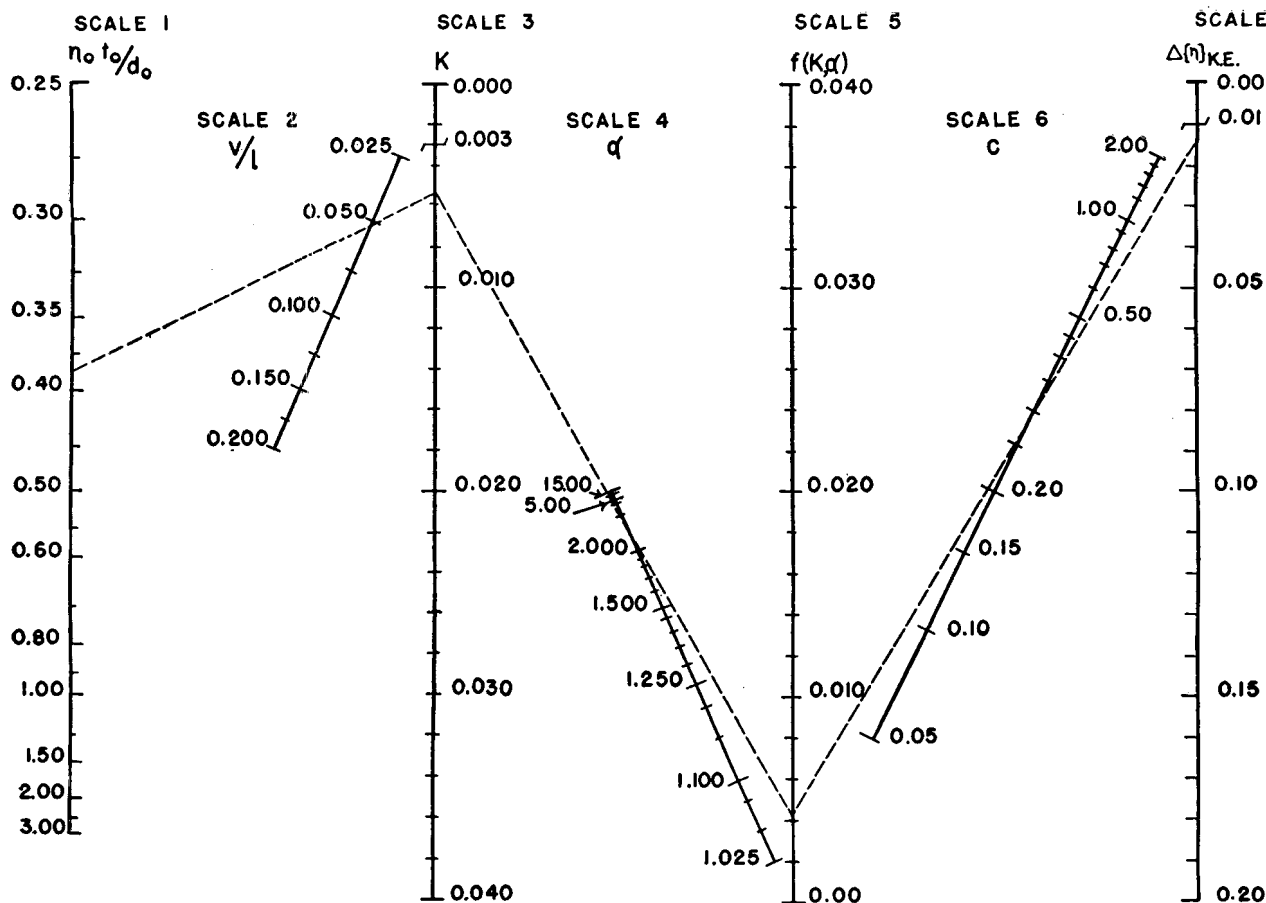
Figure 1. Nomograph for Calculating the Kinetic-Energy Contribution to the Inherent Viscosity

principle is involved in all subsequent approximations made in this paper.

To the Inherent Viscosity. The variation or uncertainty produced in the inherent viscosity, $\Delta\{\eta\}$, by a given uncertainty in the relative viscosity is:

$$\Delta\{\eta\} = \frac{\partial\{\eta\}}{\partial\eta_r} \times \Delta\eta_r = \frac{\Delta\eta_r}{\eta_r \cdot C} \qquad (6)$$

Hence we have:

$$\Delta\{\eta\}_{dens.} = \frac{\Delta\beta}{\beta \times C} \approx \frac{\Delta\beta}{C} \qquad (7)$$

by combining Equations 4 and 6.

General Considerations. It is apparent from the equations above that the magnitude of the errors will depend only upon $\Delta\beta$, C, and α, and will be completely independent of the dimensions of the viscometer. The magnitude of $\Delta\beta$ is, in general, sufficiently small so that the total error related to it is usually within the allowable uncertainty of the measurement. It can be shown that $\Delta\beta$ is the product of the solute concentration, C, and the quantity, $\frac{1}{d_0} \times \frac{\Delta d}{\Delta C}$, where $\Delta d/\Delta C$ is the slope of the density-concentration curve. This curve is essentially linear up to concentrations of at least 2.00 grams per 100 cc.; its sign and magnitude are determined by the relative magnitudes of the densities of the solute and solvent, d_s and d_0, respectively. Values of $d_s - d_0$ and $\frac{1}{d_0} \times \frac{\Delta d}{\Delta C}$ are given in Table 1 for twelve solute-solvent systems.

Absolute values of $d_s - d_0$ exceeding 0.8 are not likely to be found in practice, from which it follows that $\pm\frac{1}{d_0} \times \frac{\Delta d}{\Delta C}$ and $\pm \Delta\beta/C = 0.010$. Thus it may be concluded that the relative densities need not be taken into consideration in the viscometry of polymer solutions, provided the allowable uncertainty in the inherent viscosity is equal to or greater than 0.01 of a unit.

CONTRIBUTION OF THE KINETIC-ENERGY FACTOR

To the Relative Viscosity. This contribution is given by the second term of Equation 2 or:

$$(\Delta\eta_r)_{k.e.} = \beta K \times \frac{\alpha^2 - 1}{\alpha} \qquad (8)$$

Since β is unity to within 1 or 2%, Equation 8 may be written:

$$(\Delta\eta_r)_{k.e.} \approx K \times \frac{\alpha^2 - 1}{\alpha} \qquad (9)$$

without significant error.

To the Inherent Viscosity. By combining Equations 2 and 8 with Equation 6 the exact expression for the kinetic-energy contribution to the inherent viscosity is obtained. This expression:

$$\Delta\{\eta\}_{k.e.} = \frac{K(\alpha^2 - 1)}{[\alpha^2 + K(\alpha^2 - 1)]C} \qquad (10)$$

may be simplified to:

$$\Delta\{\eta\}_{k.e.} \approx \frac{K(\alpha^2 - 1)}{\alpha^2 C} \qquad (11)$$

since $K(\alpha^2 - 1)$ is small compared with α^2.

Table I. Density Factors of Solute-Solvent Systems at 25° C.

Solute	Solvent	Density[a] of Solute, d_s	Density of Solvent, d_0	$d_s - d_0$	$\frac{1}{d_0} \times \frac{\Delta d}{\Delta C}$
Cellulose acetate butyrate	Acetone	1.50	0.784	0.72	0.009
Cellulose acetate	Acetone	1.35	0.784	0.57	0.006
Polyvinyl acetate	Acetone	1.19	0.784	0.42	0.007
Polyvinyl acetate	Benzene	1.19	0.873	0.33	0.006
Polyvinyl alcohol	Water	1.30	0.997	0.30	0.002
Gelatin	Water	1.27	0.997	0.27	0.003
Polystyrene	Benzene	1.06	0.873	0.19	0.002
Ethylcellulose	Dioxane	1.15	1.032	0.12	0.001
Rubber (natural)	Toluene	0.91	0.860	0.05	0.001
Polyisobutylene	Benzene	0.95	0.873	0.08	0.000
Polyisobutylene	Chloroform	0.95	1.469	-0.52	-0.004
Rubber (natural)	Chloroform	0.91	1.469	-0.56	-0.005

[a] Solute density values were obtained from tables in Meyer's book (2); and from data given by Wearmouth (4).

Table II. K Values Required to Produce a $\Delta\{\eta\}_{k.e.} = 0.010$

Inherent Viscosity	Concentration, Grams per 100 Cc.				
	0.125	0.250	0.500	1.000	2.000
0.10	0.051	0.051	0.053	0.055	0.060
0.25	0.021	0.021	0.023	0.025	0.032
0.50	0.011	0.011	0.013	0.016	0.023
1.00	0.006	0.006	0.008	0.012	0.020
1.50	0.004	0.005	0.006	0.011	0.020
2.00	0.003	0.004	0.006	0.010	0.020
2.50	0.003	0.004	0.005	0.010	0.020
3.00	0.002	0.003	0.005	0.010	0.020
3.50	0.002	0.003	0.005	0.010	0.020
4.00	0.002	0.003	0.005	0.010	0.020
4.50	0.002	0.003	0.005	0.010	0.020
5.00	0.002	0.003	0.005	0.010	0.020

General Considerations. In order to minimize the magnitude of the kinetic-energy correction, conditions should be provided which will produce the lowest practicable value of K. The factor $V/8\pi l$ of K (see Equation 2) is determined by the dimensions of the viscometer; a well-designed instrument should have as small a ratio of V/l as possible consistent with size and operational requirements. The magnitude of the remaining factor of K will depend on the kinematic viscosity, η_0/d_0, of the solvent, and its outflow time, t_0. The choice of solvent, and hence the kinematic viscosity, is usually fixed by solubility considerations. The magnitude of the outflow time can, for a given solvent, be adjusted between fairly wide limits by choosing the capillary bore and the average pressure head to be used in the viscometer (initial design). Very large values of t_0 should be avoided, however, as a method of minimizing K, since any advantage thus derived will be offset by the excessive time required in making measurements.

To facilitate the evaluation of K from known or given values of η_0, d_0, t_0, V, and l; and also of $\Delta\{\eta\}_{k.e.}$, from K, α, and C, a nomograph, shown as Figure 1, has been prepared. Its use should be readily understood by the following example, shown in Figure 1 as a broken line:

The kinematic viscosity of acetone at 25° C. of 0.0038 stoke, combined with the experimentally found value of 100 seconds for t_0, yields, on Scale 1, the indicated quantity. For an instrument whose V/l is 0.053 sq. cm., we obtain K equal to 0.055 on Scale 3. If the ratio of efflux times, α, is 2.500 for a solution containing 0.300 gram per 100 cc., a value of $\Delta\{\eta\}_{k.e.} = 0.015$ is indicated. This quantity, if significant, should be added to $\ln \alpha/C$.

The nomograph may be used in the reverse direction to determine the required conditions if the kinetic-energy factor is to be kept within a certain predetermined maximum. To this end the following procedure should be adopted: The maximum allowable value of $\Delta\{\eta\}_{k.e.}$ and the minimum concentration of solution planned to be used are aligned to produce a point on Scale 5. This point is then aligned with the maximum value of α likely to

be obtained at the afore-mentioned minimum concentration to ascertain the required value of K. Table II, which gives values of K required to make $\Delta\{\eta\}_{k.e.}$ equal to 0.01 for various inherent viscosities at various concentrations, should be helpful in estimating this maximum α. The various combinations of $\eta_0 t_0/d_0$ and V/l necessary to produce this K can be readily determined. The use of the nomograph in this capacity is most useful in the designing of new viscometers.

In determining the optimum dimensions of a viscometer to be used in polymer measurement, the dimensions should be based upon the characteristics of the solvent of minimum (kinematic) viscosity likely to be employed. A viscometer so designed when used with solvents of greater viscosity will give rise to increasingly smaller kinetic-energy errors.

COMBINED EFFECTS

Fully corrected values of the relative viscosity and of the inherent viscosity can be calculated from the quantities α, C, β, and K by means of the following equations:

$$\eta_r = \alpha \left[1 + \Delta\beta + (2\Delta\beta + 1) \times K \times \frac{\alpha^2 - 1}{\alpha^2} \right] \approx \quad (12)$$

$$\alpha \left[1 + \Delta\beta + K \times \frac{\alpha^2 - 1}{\alpha^2} \right]$$

$$\{\eta\} = \frac{\ln \alpha}{C} + \frac{\alpha^2 \Delta\beta + (2\Delta\beta + 1) \times K \times (\alpha^2 - 1)}{\left[\alpha^2 + K(\alpha^2 - 1) \right](\Delta\beta + 1)C} \approx \quad (13)$$

$$\frac{\ln \alpha}{C} + \frac{\Delta\beta}{C} + \frac{K(\alpha^2 - 1)}{\alpha^2 C}$$

Table III illustrates typical results obtained with viscometers of different dimensions. These serve as examples of the magnitude of the correction factors for polymers of four representative viscosities.

Table III.   Typical Data Obtained with Different Viscometers

(System: polyvinyl acetates in acetone, $\Delta\beta = 0.007$ C. Viscometer 1, $K = 0.0375$; viscometer 2, $K = 0.0067$)

Polymer	C, G/100 Cc.	α	$\frac{\ln \alpha}{C}$	$\frac{\Delta\beta}{C}$	$\frac{K}{C} \times \frac{\alpha^2 - 1}{\alpha^2}$	$\{\eta\}$
	Viscometer 1					
Low viscosity, [η] = 0.16	0.525	1.083	0.15	0.007	0.011	0.17
	1.050	1.163	0.14	0.007	0.009	0.16
Medium viscosity [η] = 1.00	0.250	1.257	0.92	0.007	0.058	0.98
	0.500	1.559	0.89	0.007	0.045	0.94
	1.000	2.257	0.81	0.007	0.029	0.85
High viscosity [η] = 2.76	0.250	1.847	2.36	0.007	0.110	2.48
	0.500	2.925	2.15	0.007	0.068	2.22
	1.000	6.026	1.80	0.007	0.037	1.84
Very high viscosity [η] = 4.75	0.240	2.594	3.97	0.007	0.134	4.11
	0.490	5.372	3.43	0.007	0.074	3.51
	1.000	13.868	2.63	0.007	0.038	2.67
	Viscometer 2					
Low viscosity [η] = 0.16	0.525	1.08	0.16	0.007	0.004	0.17
	1.050	1.172	0.15	0.007	0.002	0.16
Medium viscosity [η] = 1.00	0.250	1.270	0.96	0.007	0.010	0.98
	0.500	1.584	0.92	0.007	0.008	0.94
	1.000	2.320	0.84	0.007	0.005	0.85
High viscosity [η] = 2.76	0.250	1.852	2.46	0.007	0.018	2.48
	0.500	3.000	2.20	0.007	0.011	2.22
	1.000	6.185	1.82	0.007	0.006	1.84
Very high viscosity [η] = 4.75	0.240	2.661	4.08	0.007	0.024	4.11
	0.490	5.534	3.49	0.007	0.013	3.51
	1.000	14.200	2.66	0.007	0.007	2.67

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Oxide Films Formed on Titanium, Zirconium, and Their Alloys with Nickel, Copper, and Cobalt

An Electron Diffraction Study

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The electron diffraction technique is used to study the structures of the oxides which form on the metals, titanium and zirconium, and on the alloys, 50 Ti-Ni, 70 Ti-Ni, 28 Ti-Cu, 20 Zr-Cu, 60 Zr-Co, and 70 Zr-Ni, in the temperature range 300° to 700° C. The structures found are plotted on existence diagrams as functions of time and temperature. Attempts are made to correlate the structures obtained with thermodynamic data reported by other workers. The oxides occurring on titanium and zirconium are titanium dioxide (rutile) and the monoclinic modi-

fication of zirconium oxide, respectively. Titanium displays greater oxidation resistance than zirconium, which shows evidence of solid solubility of the oxide in the metal. Titanium-nickel alloys show only the presence of rutile, while the titanium-copper alloy yields cuprous oxide below 500° C. and rutile above 500° C. Zirconium alloys do not show the presence of zirconium dioxide, even though thermodynamic data indicate that it should be observed. Zirconium ion appears to have lower rates of formation and diffusion than cobalt, copper, and nickel ions.

THE determination of the structures of the surface oxides resulting from a gas-metal reaction is one of the important factors in understanding the mechanism of the reaction. If these determinations are carried out in a consistent and systematic manner in regard to time, temperature, and gas pressure, a good deal of information may be obtained concerning the relative importance of the formation and diffusion of the several metal ions or the formation and diffusion of the oxygen ion, atom, or molecule through the oxide film. In addition, it may be possible to check on the thermodynamic predictions of possible oxide structures formed on the metal or alloy as well as reactions between the oxides in the film.

The authors (9, 11) have presented electron diffraction investigations of the oxides which form on iron, cobalt, nickel, chromium, copper, tungsten, and molybdenum. This communication reports a similar study on titanium and zirconium and their alloys with nickel, copper, and cobalt.

Titanium and zirconium are reported (13) to react with hydrogen, nitrogen, and oxygen at elevated temperatures. Neither metal forms tarnish films in air and both metals are considered protective up to 500° C. The corrosion resistance of both metals is excellent according to Hoyt (13), with zirconium resisting nitric and hydrochloric acids in all concentrations up to 100° C. and hot 50% sulfuric acid. Recent advances (15) in the metallurgy of these metals may result in increased use in corrosion-resistant applications.

Titanium has been used in some alloys for high-temperature service in gas turbines (4). Zirconium has found uses as a minor constituent in high-temperature heater alloys (16).

The authors' interest in the study of the oxidation of these metals and their alloys with nickel, copper, and cobalt is a result of the following facts:

Titanium and zirconium have moderately high melting points and zirconium forms a very refractory oxide.
The oxides of titanium and zirconium are extremely stable thermodynamically with respect to reactions with the alloying metals nickel, copper, and cobalt.
The metals are not protective above 500° C.
The x-ray diffraction data for the several systems in the bulk state have been determined.

SURVEY OF LITERATURE

The metals, titanium and zirconium, are hexagonal close-packed at room temperature but transform to body-centered cubic modifications at approximately 860° C. When the metals

are produced from the gas phase, they are highly ductile and malleable.

The titanium-oxygen system was investigated by Ehrlich (5) who found four phases. The system was investigated by heating mixtures of titanium dioxide and titanium metal. An alpha phase ($TiO_{2.00}$ to $TiO_{1.90}$) probably has a deformed rutile lattice. The gamma phase ($TiO_{1.56}$ to $TiO_{1.46}$) corresponds to the compound Ti_2O_3 and has a structure of the corundum type. The delta phase ($TiO_{1.25}$ to $TiO_{0.6}$) has the sodium chloride structure with a lattice parameter of 4.165 Å. From $TiO_{1.33}$ to $TiO_{0.69}$ the lattice constant decreases linearly.

Various oxides of titanium which occur in nature as minerals have been investigated by x-ray diffraction. Among these are the three crystalline modifications of titanium dioxide: rutile and anatase which are tetragonal and brookite which has an orthorhombic structure. These three modifications may be prepared artificially. Anatase is reported (18) to exist in two modifications; anatase II transits to anatase I at 642° C. Anatase I is stable up to 915° C. where rutile becomes the stable modification. At 1300° C. rutile transits to brookite which melts at 1900° C. The monoxide, TiO, may be prepared from the dioxide by high-temperature reduction with carbon or magnesium. Its melting point is 1750° C.

At moderate temperature (210° C.) finely powdered zirconium will burst into flame when heated in air. Marden and Rich (17) found that a piece of the compact metal can be heated to bright redness in the blast furnace with no more than a thin, bluish superficial oxidation. Hoyt (13) states that both oxygen and nitrogen dissolve in zirconium, so that the metal cannot be used above 500° C. in the presence of either gas. It will also dissolve increasingly large amounts of hydrogen as the temperature is elevated, except that at 860° C. (the transformation temperature) the solubility decreases markedly. This behavior of hydrogen is reported to be reversible.

The metal forms the dioxide, ZrO_2, which is reported to exist in at least three crystalline modifications: monoclinic (10), cubic (3), and tetragonal (19). All three modifications have been investigated by x-ray diffraction. In addition, two oxides of lower oxidation states have been reported but the evidence in favor of these is doubtful. Cohn and Tolksdorf (3), who investigated the stabilities of the zirconium oxides, found the monoclinic modification stable to 1000° C. while the tetragonal modification is stable above 1000° C. and may be cooled to room temperature. The trigonal or pseudo-hexagonal modification forms after long
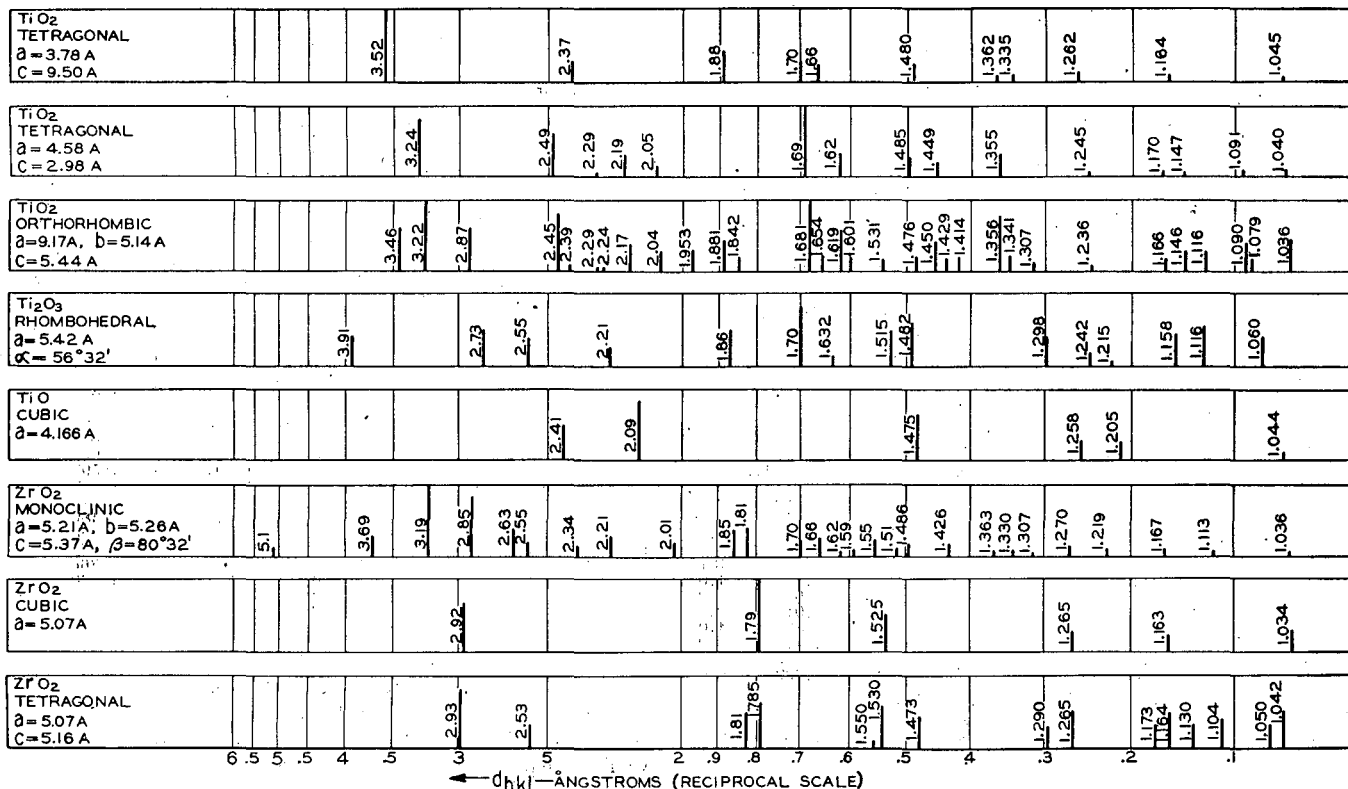
Figure 1. Experimental Diffraction Patterns of Titanium and Zirconium Oxides

continuous heating at temperatures higher than 1900° C. They also noted a transition point at 625° C. when the trigonal modification is cooled.

Both titanium and zirconium dioxides react with metal oxides in the solid phase at high temperatures to form titanates and zirconates. One of these systems has been studied by Taylor (20), who prepared $NiTiO_3$ by heating nickel oxide and titanium dioxide at 900° C. for 39 hours. The resultant product gave x-ray diffraction lines of NiO, $NiTiO_3$, and Ni_2TiO_4. In the oxidation of binary alloys of titanium or zirconium there is a possibility that solid phase reactions between the various metal oxides may occur.

SAMPLE PREPARATION AND METHOD

When the reflection electron diffraction technique is used to study oxide surfaces, the preparation of the metallic surface prior to oxidation is important in determining the quality of the patterns obtained. Experiments have shown that a clean, flat, slightly matted surface, which can be penetrated by the electrons, gives sharp, intense patterns.

Samples are prepared by machining or grinding to dimensions of 0.375-inch length and 0.375-inch diameter. These are given a surface finish with a precision abrader (8) ending up with 4/0 emery paper. Oxidations are carried out in the diffraction camera without any other pretreatment such as annealing. Purified oxygen under approximately 1-mm. pressure is used as the oxidizing agent. Diffraction patterns are taken at high temperature in the vacuum of the camera before oxidation; after 1, 5, 30, and 60 minutes' oxidation; and after cooling to room temperature under approximately 0.05-atmosphere pressure of hydrogen. Hydrogen is used to enhance the cooling rate.

The interplanar distances obtained from the diffraction patterns are compared with those reported by other workers using x-ray diffraction. The data from the oxidations are plotted in the form of existence diagrams of the oxides on a time-temperature scale (Figures 2 to 9). The diffraction patterns are classified as oriented, sharp, medium, and diffuse. These classifications refer to the types of patterns and are represented by the

letters O, S, M, and D, respectively, on the existence diagrams. If intense arcs or spots occur on a pattern as a result of preferential growth of the oxide on the surface of the metallic substrate, the pattern is classified "oriented." The classifications sharp, medium, and diffuse are made on the basis of the width of the diffraction lines.

The titanium used in this study has the following analysis: Ti (94 to 98%), H_2 (0.0 to 0.1%), C (0.0 to 0.5%), N_2 (0.7 to 0.9%), Fe (0.02 to 0.7%), Si (0.0 to 1.5%), Al (0.03%), Zr (0.1%), and Ca (0.1%).

The zirconium has the following analysis: Zr (95.0 to 99.5%), H_2 (0.01%), C (0.3%), and Si (0.3%).

The alloys are not analyzed but the percentages given are those used in their preparation, starting with titanium and zirconium with analyses as given above.

The samples used in this study were obtained from Metal Hydrides, Inc., Beverly, Mass.

RESULTS

Figure 1 lists the interplanar distances and relative intensities of the diffraction lines for the oxides of titanium and zirconium as determined by x-ray diffraction by other workers.

Table I gives a synopsis of the results presented more completely in graphical form in the existence diagrams (Figures 2 to 9). Tables II to V show the results obtained when the samples are oxidized in a tube furnace in an oxygen atmosphere. With the exception of zirconium, all samples were oxidized for 1 hour at 700° C. In the case of zirconium oxidation was carried out at 500° C. In Tables II to V card numbers which contain no Roman numeral prefix are taken from (1), while those containing a Roman prefix are from (2).

Titanium. Table II shows that the results obtained by reflection electron diffraction from the surface and by x-ray examination of the oxide after removal from the substrate indicate the presence of titanium dioxide in the form of rutile on titanium. This is not in agreement with the report (18) that anatase should be the oxide obtained below 915° C. The regions of

Table I. Oxides Found on Metals and Alloys

Metal or Alloy	Fig.	Temp., °C.	Oxidation Time, Min.	Oxide Structure
Titanium	2	300–700	1–60	TiO_2 (rutile)
Zirconium	3	300–600	1–60	ZrO_2 (monoclinic)
50 Ti-Ni	4	300–700	1–60	TiO_2 (rutile)
70 Ti-Ni	5	300–700	1–60	TiO_2 (rutile)
28 Ti-Cu	6	300–700	1–60	$Cu + Cu_2O$ at 300° to 400° C. (1–5 min.) Cu_2O at 300–400° C. (30–60 min.) TiO_2 (rutile) at 500–700° C.
20 Zr-Cu	7	300–700	1–60	Cu_2O at 300–400° C. Cu_2O at 500° C. (1–5 min.) CuO (30–60 min.) CuO at 600–700° C.
60 Zr-Co	8	300–700	1–60	Co_3O_4 at 300–700° C.
70 Zr-Ni	9	300–700	1–60	NiO at 300–700° C.

Table II. Experimental Interplanar Distances of Rutile

X-ray spectrometer		Electron diffraction		Rutile Card 3653		Card II, 1089	
d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I
3.257	10.0	3.22	4.0	3.24	8.0	3.24	10.0
2.498	3.5	2.50	3.0	2.49	6.0	2.49	7.0
...	...	2.29	5.0	2.29	0.4	2.31	2.0
						2.26	3.0
2.195	1.0	2.17	3.0	2.19	3.0	2.19	4.0
...	...	2.06	3.0	2.05	1.2	2.05	3.0
...	...	...	...	...	...	2.01	2.0
...	...	...	...	...	...	1.877	4.0
...	...	...	...	...	...	1.779	2.0
1.689	4.0	1.68	10.0	1.69	10.0	1.682	10.0
1.624	0.5	1.63	1.0	1.62	3.0	1.622	6.0
...	...	...	...	...	...	1.500	2.0
...	...	1.48	4.0	1.485	2.0	1.470	2.0
...	...	...	...	1.449	2.0	1.450	4.0
1.360	0.5	1.365	6.0	1.355	3.0	1.357	8.0
...	...	...	...	1.245	0.4	...	...
...	...	...	...	1.170	0.8	...	...
...	...	1.155	3.0	1.147	0.4	...	...
...	...	1.108	2.0	1.091	0.8	...	...
...	...	1.037	3.0	1.040	0.8	...	...
...	...	0.973	1.0	0.964	0.4	...	...
...	...	...	...	0.903	0.2	...	...
...	...	0.884	2.0	0.890	0.8	...	...
...	...	...	...	0.875	0.4	...	...
...	...	...	...	0.843	0.2	...	...
...	...	...	...	0.832	0.4	...	...
...	...	0.816	1.0	0.822	0.4	...	...

d, interplanar distance, Å.
I, visually measured intensity on arbitrary scale of 10.

Table III. Experimental Interplanar Distances of Zirconium Dioxide

X-ray spectrometer		Electron diffraction		Zirconium Dioxide (Monoclinic) Card 1812		Card II, 1018		Card II, 1163	
d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I
...	...	...	...	5.12	0.5	...	...	...	...
3.67	1.6	3.69	1	3.69	2.4	3.71	2.0	3.69	5.0
						3.34	10.0		
3.15	10.0	3.17	7	3.19	10.0	...	...	3.18	10.0
2.84	9.0	2.85	6	2.85	8.0	2.95	7.0	2.85	10.0
						2.69	6.0		
2.63	2.5	2.63	2	2.63	3.2	...	...	2.63	7.0
2.54	2.4	2.54	2	2.55	1.6	...	...	2.55	5.0
...	...	...	...	2.34	0.8	...	...	2.34	2.0
...	...	...	...	...	...	2.24	6.0	2.23	5.0
2.21	2.0	2.20	1	2.21	2.4	...	...	2.20	5.0
2.02	1.0	...	...	2.01	1.6	2.03	6.0	2.01	5.0
								1.99	5.0
1.84	4.0	1.85	4	1.85	3.2	1.845	10.0	1.852	10.0
1.81	4.0	1.81	4	1.81	4.0	...	...	1.814	10.0
...	...	...	...	1.70	2.0	1.712	7.0	1.695	7.0
1.66	2.5	...	...	1.66	2.4	1.671	5.0	1.658	7.0
...	...	...	...	1.62	0.5	...	...	1.621	6.0
...	...	...	...	1.59	9.6	1.604	2.0	1.593	5.0
1.54	1.8	...	...	1.55	2.4	1.561	5.0	1.549	7.0
...	...	...	...	1.51	0.8	1.504	7.0	1.512	5.0
1.47	1.7	...	...	1.486	1.6	...	...	1.486	6.0
								1.453	2.0
1.426	1.2	...	...	1.426	1.6	1.434	5.0	1.427	6.0
...	...	...	...	1.363	0.5	1.371	...	1.366	5.0
...	...	...	...	1.330	0.8	1.334	...	1.330	6.0
...	...	...	...	1.307	0.3	...	...	1.309	5.0

be very oxidation-resistant, since the oxide films show interference colors and are removed with difficulty. The oxide film is easily removed from 28 Ti-Cu, indicating that oxide scaling would take place readily. The samples for transmission patterns are prepared by grinding the removed film in an agate mortar and allowing a water suspension of this finely divided powder to settle on a thin film of Parlodion stretched over an electron microscope specimen screen. All the transmission patterns are characterized by being more diffuse than those obtained by reflection. Inspection of the powdered particles with an optical microscope (100 ×) shows the particle size to be rather large. The diffuse patterns, however, may be caused by the particles being composed of very fine crystals which do not diffract cooperatively. While the

stability of the various modifications of titanium dioxide are probably influenced by the presence of the metallic substrate. In order to determine whether any difference may be noted when the substrate is not present, a sample of finely divided titanium powder (200 mesh) was oxidized under identical conditions. This, too, gave a pattern of rutile. It is evident that further work on the oxidation of titanium powder and the stability of the oxides formed is required. The authors intend to present a report on this work at some future date.

Zirconium. Table III shows that the oxide obtained when zirconium is oxidized at 500° C. is the monoclinic modification of zirconium dioxide. The oxide, which adheres very tenaciously to the metal, is removed with difficulty. This may substantiate the report of Fast and Jacobs (6) that zirconium dissolves large quantities of oxygen, since a solid solution of metal and oxide probably occurs at the interface. A sample of zirconium powder (200 mesh) oxidized under the same conditions as the zirconium rod also shows the presence of monoclinic zirconium dioxide. The cubic and tetragonal forms are not observed. Both results are in agreement with the report of Cohn and Tolksdorf (3), who found the monoclinic modification stable below 1000° C.

Titanium Alloys. Table IV shows the results obtained when rods of the titanium alloys are oxidized for one hour at 700° C. Both the reflection and transmission electron diffraction data indicate that titanium dioxide (rutile) is the only oxide present on the surface of 50 Ti-Ni, 70 Ti-Ni, and 28 Ti-Cu. In order to obtain sufficient samples of oxides for transmission diffraction and spectrographic analyses, the oxide films were scraped off the substrate with a steel spatula. The 50 Ti-Ni and 70 Ti-Ni alloys appear to

Figure 2. Oxide Films on Titanium at 1 Mm. of Oxygen for Various Times and Temperatures

Table IV. Electron Diffraction Patterns of Oxides on Titanium Alloys

50 Ti-Ni				70 Ti-Ni				28 Ti-Cu				TiO (Rutile)			
Reflection		Transmission		Reflection		Transmission		Reflection		Transmission		Card 3653		Card II, 1089	
d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I
3.26	6	...	...	3.26	4	...	...	3.23	3	3.23	2	3.24	8.0	3.24	10.0
2.46	4	2.47	3	2.50	2	2.47	4	2.47	8	2.46	6	2.49	6.0	2.49	7.0
...	...	...	...	...	...	...	...	...	...	...	...	2.29	0.4	2.31	2.0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	2.26	3.0
2.17	2	2.20	2	2.18	2	2.18	2	2.17	5	2.15	4	2.19	3.0	2.19	4.0
2.06	3	2.07	1	...	...	...	...	...	...	...	...	2.05	1.2	2.05	3.0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	2.01	2.0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	1.877	4.0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	1.779	2.0
1.694	6	1.68	5	1.685	3	1.674	5	1.69	8	1.664	7	1.69	10.0	1.682	10.0
...	...	...	...	...	...	...	...	...	...	...	...	1.62	3.0	1.622	6.0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	1.500	2.0
1.474	4	1.474	4	1.465	2	1.475	4	1.485	6	...	...	1.485	2.0	1.470	2.0
...	...	...	...	...	...	...	...	...	...	...	...	1.449	2.0	1.450	4.0
1.353	3	1.355	2	1.346	2	1.355	2	1.360	5	1.345	3	1.355	3.0	1.357	8.0
...	...	...	...	...	...	...	...	...	...	...	...	1.245	0.4	...	...
1.184	2	...	...	...	...	...	...	1.185	1	...	...	1.170	0.8	...	...
...	...	...	...	...	...	...	...	...	...	...	...	1.147	0.4	...	...
1.098	1	...	...	...	...	...	...	1.093	1	...	...	1.091	0.8	...	...
1.035	2	...	...	...	...	...	...	1.048	1	...	...	1.040	0.8	...	...
0.956	1	...	...	...	...	...	...	0.950	2	...	...	0.964	0.4	...	...
...	...	...	...	...	...	...	...	...	...	...	...	0.903	0.2	...	...
...	...	...	...	...	...	...	...	0.877	2	...	...	0.890	0.8	...	...

oxide was present on the substrate sharp patterns resulted, indicating there must have been projections of good diffracting crystals in sufficient numbers to diffract cooperatively. The diffraction results are not in complete agreement with the spectrographic analyses which show the presence of both metals in the oxide films. The spectrographic analyses, which are qualitative, indicate that the alloying metals are present in much smaller amounts in the oxide films than in the alloys. Further work is required to determine the quantitative limits of concentration of one oxide in the presence of another oxide which may be detected by the diffraction method.

Zirconium Alloys. Table V shows the results obtained with the zirconium alloys. The oxide film on 20 Zr-Cu consists of cupric oxide in the outer layer with cuprous oxide underneath in contact with the substrate. This alloy oxidizes readily and would scale with slightly longer oxidation time. Spectrographic analysis shows a trace of zirconium present in the oxide. No transmission data are given for 60 Zr-Co and 70 Zr-Ni, since the oxide films could not be removed from the substrates. The reflection data show the presence of cobalto-cobaltic oxide and nickel oxide on 60 Zr-Co and 70 Zr-Ni, respectively. The absence of zirconium oxide in the surface layer is a further indication that this oxide may be in contact with the substrate at the interface. The 70 Zr-Ni alloy is the only nickel-containing alloy thus far examined in this laboratory which shows the presence of nickel oxide in the outer surface of the oxide layer at temperatures greater than 500° C.

DISCUSSION

Free Energies and Equilibrium Constants. Table VI gives a synopsis of thermodynamic data, based on original information taken from Thompson (21). The values given under the several temperatures are equal to $\log_{10} K_R$, where

$$\Delta F_R^{\circ} = -RT \ln K_R$$

and

$$\frac{\Delta F_R^{\circ}}{-4.575T} = \log_{10} K_R$$

ΔF_R° and K_R are the free energy and equilibrium constants of the reaction. The several reactions are arranged in the order of decreasing values of $\log_{10} K_R$. Table VI may be used to determine whether a given solid phase reaction is possible thermodynamically.

An inspection of Table VI shows that zirconium will reduce all the other metallic oxides listed. This can occur only if the rates of formation and diffusion of zirconium ions are high enough to permit the occurrence of solid phase reactions. Since it is known that oxygen is soluble in zirconium, it is possible that zirconium ions may not get to the surface and take part in reducing reactions.

Titanium. Figure 2 shows that the rutile modification of titanium dioxide is the oxide obtained over the complete time-temperature range. The observations indicate that titanium in rod form does not oxidize very rapidly in the temperature range under consideration. The existence diagram shows that physical differences exist in the oxide films as a function of temperature. In general, the patterns become sharper as the temperature is elevated.

Although the dioxides of titanium should form in the order anatase, rutile, and brookite as a function of the elevation of temperature, the results indicate that rutile is the stable modification when the oxide is in contact with the substrate. This is in agreement with the observation that crystals of brookite and anatase have been found that have transformed to rutile. Furthermore, the oxidation of titanium powder gave only rutile as evidenced by the x-ray diffraction results.

Table V. Electron Diffraction Patterns of Oxides on Zirconium Alloys.

20 Zr-Cu				CuO, Card 2857		Cu₂O, Card 2928		60 Zr-Co, Reflection		Co₃O₄, Card 2953		70 Zr-Ni, Reflection		NiO, Card 3309	
Reflection		Transmission													
d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I	d, Å.	I
2.53	5	...	...	2.51	10.0	...	...	...	...	4.68	0.8	2.40	4	2.40	6.0
...	...	2.45	5.0	...	...	2.45	10.0	2.91	4	2.86	2.0	2.09	7	2.08	10.0
2.31	8	...	...	2.31	10.0	...	...	2.45	7	2.43	10.0	1.481	7	1.474	6.0
...	...	2.10	2.0	...	...	2.12	3.1	...	...	2.34	0.6	1.270	3	1.258	2.4
1.96	1	...	...	...	...	...	...	2.05	2	2.02	1.3	1.218	1	1.203	1.2
1.87	3	...	...	1.85	2.0	...	...	1.635	2	1.65	0.4	1.040	1	1.042	0.2
...	...	...	...	1.70	0.8	...	...	1.575	4	1.56	2.5	...	...	0.957	0.4
1.59	5	...	...	1.57	0.8	...	...	1.428	4	1.432	3.0	...	...	0.933	0.6
1.51	6	1.50	3.0	1.50	1.5	1.51	4.4	1.254	2B	1.235	0.2	...	...	0.852	0.3
1.395	5	...	...	1.408	2.0	...	...	...	...	1.084	0.1	...	...	0.802	0.2
1.361	4	...	...	1.370	2.0	...	...	1.065	2B	1.055	0.4	...	...	...	...
1.295	3	...	...	1.298	0.5	...	...	...	...	1.012	0.1	...	...	...	...
...	...	1.277	2.0	...	...	1.283	3.1	...	...	0.931	0.2	...	...	...	...
1.270	3	...	...	1.258	1.0	1.228	0.5	...	...	0.850	0.1	...	...	...	...
1.166	3	...	...	1.159	0.5	...	...	...	...	0.828	0.2	...	...	...	...
...	...	...	...	1.086	0.3	...	...	...	...	...	...	...	...	...	...
...	...	...	...	1.007	0.3	...	...	...	...	...	...	...	...	...	...
0.966	3	...	...	0.978	0.3	0.977	0.5	...	...	...	...	...	...	...	...
0.885	3	...	...	0.885	0.3	0.953	0.3	...	...	...	...	...	...	...	...
...	...	...	...	...	...	0.869	0.3	...	...	...	...	...	...	...	...
...	...	...	...	...	...	0.819	0.3	...	...	...	...	...	...	...	...

Table VI. Free Energies of Formation of Oxides

Units of $\dfrac{\Delta F_R°}{-4.575}$

Reaction	Temperature, ° C.					
	200	300	400	500	600	700
Zr (s) + O₂ (g) ⇌ ZrO₂ (s)	110.2	89.5	75.0	64.7	56.3	49.2
Ti (s) + O₂ (g) ⇌ TiO₂ (s)	91.2	73.8	61.4	52.2	45.2	39.6
3 Co (s) + 2 O₂ (g) ⇌ Co₃O₄ (s)	75.5	59.7	48.4	40.0	33.5	28.1
Ni (s) + 0.5 O₂ (g) ⇌ NiO (s)	23.0	18.9	14.7	12.2	10.2	8.65
Co (s) + 0.5 O₂ (g) ⇌ CoO (s)	22.1	17.7	14.5	12.14	10.32	8.91
2 Cu (s) + 0.5 O₂ (g) ⇌ Cu₂O (s)	15.05	11.80	9.53	7.87	6.60	5.48
Cu (s) + 0.5 O₂ (g) ⇌ CuO (s)	12.4	9.42	7.53	5.82	4.65	3.75

The results also indicate that titanium dioxide is not readily reduced to titanium sesquioxide by hydrogen below 700° C. according to the reaction:

$$2\ TiO_2\ (s) + H_2\ (g) \rightleftharpoons Ti_2O_3\ (s) + H_2O\ (g) \tag{1}$$
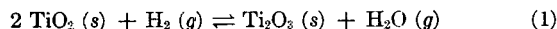
This is in agreement with the results reported by Goldschmidt and co-workers (7).

It is also evident that the formation of titanium sesquioxide and titanium monoxide, which occur when titanium dioxide and titanium are heated together according to Ehrlich (5), does not take place below 700° C. when the oxide is in contact with the metallic substrate. These oxides could be formed if the following solid phase reactions occurred:

$$Ti\ (s) + 3\ TiO_2\ (s) \rightleftharpoons 2\ Ti_2O_3\ (s) \tag{2}$$

$$Ti\ (s) + TiO_2\ (s) \rightleftharpoons 2\ TiO\ (s) \tag{3}$$
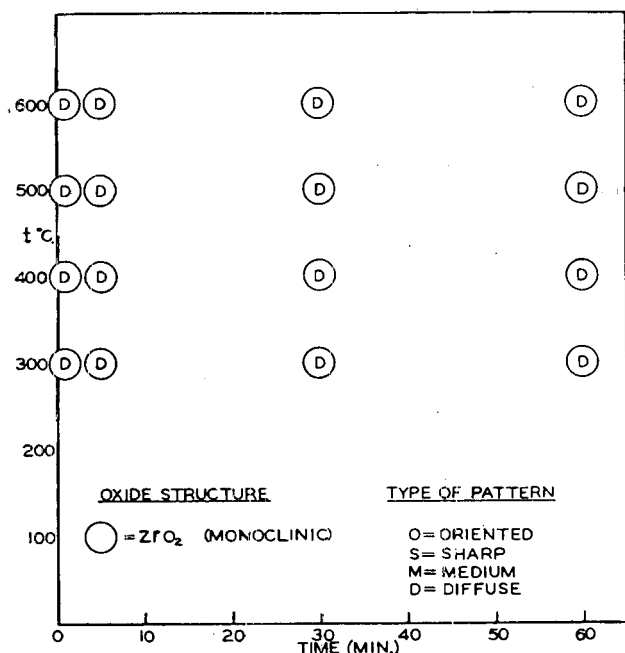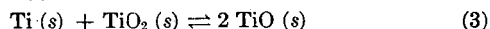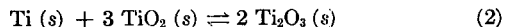
Figure 3. Oxide Films on Zirconium at 1 Mm. of Oxygen for Various Times and Temperatures

Since Ehrlich (5) did obtain the sesqui- and monoxides, their formation is possible thermodynamically in the temperature range he used. The fact that they are not observed in this work may mean that titanium ions are not forming and diffusing into the oxide to take part in the solid phase reactions.

Zirconium. Figure 3 shows that the monoclinic modification of zirconium dioxide is obtained over the complete time-temperature range. Preliminary experiments in an auxiliary furnace indicated that the bulk metal could not be oxidized safely above
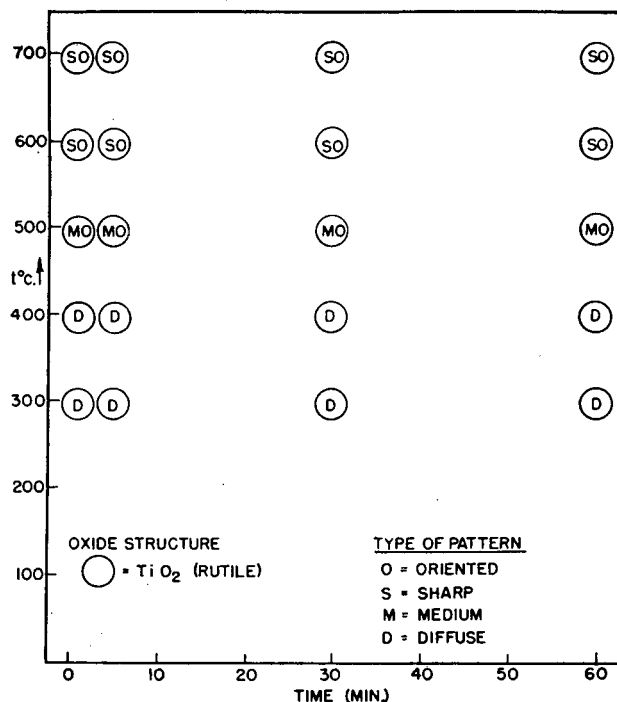
Figure 4. Oxide Films on 50 Ti-Ni at 1 Mm. of Oxygen for Various Times and Temperatures

600° C., since disintegration of the samples occurs at 650° C. It appears, therefore, that zirconium has less oxidation resistance than titanium, since the latter metal withstood oxidation well at 700° C.

The oxide films adhered very tenaciously to the substrate and gave no evidence of interference colors even for short oxidation times at low temperatures. This may indicate that the oxidation rate even at low temperatures is so high that the oxide film thickness lies beyond the interference color range or the oxide may be going into solution in the metallic substrate. The latter explanation seems more reasonable, however, since the characteristic white or yellow color of zirconium dioxide is not evident and the oxide films could not be removed readily from the metal. In addition, the diffraction patterns are diffuse even when the oxide is at elevated temperatures. This may be caused by the solubility of the oxide in the metal. Preliminary work (12) on columbium and tantalum gives evidence of the same effect.

50 Ti-Ni and 70 Ti-Ni. Figures 4 and 5 show that rutile is obtained on these alloys over the complete time-temperature range. Both alloys show oxide interference colors after 60 minutes' oxidation at 700° C. No oxide of nickel is observed. This is in agreement with the thermodynamic data of Table VI, since nickel oxide would be reduced according to the following reaction:

$$Ti\ (s) + 2\ NiO\ (s) \rightleftharpoons TiO_2\ (s) + 2\ Ni\ (s) \tag{4}$$
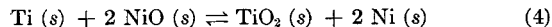
where $K_R = 10^{+36.0}$ at 300° C. and $10^{+22.3}$ at 700° C.

The experimental data cannot determine whether nickel gets to the surface, is oxidized, and subsequently reduced by titanium but they do show that either nickel ion has lower rates of formation and diffusion than titanium ion or that a solid phase reaction between nickel oxide and titanium takes place according to Equation 4.

Another type of solid phase reaction may occur on the surface if both nickel oxide and titanium oxide are coexistent there. These reactions may be illustrated as follows:
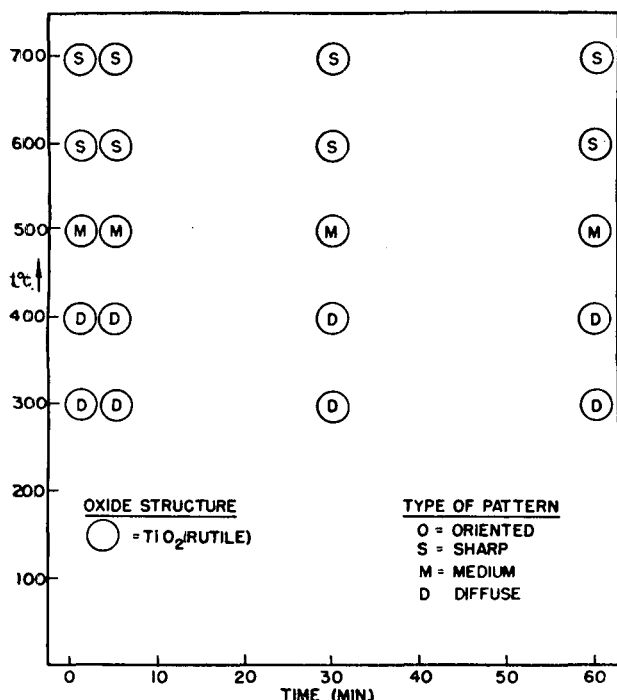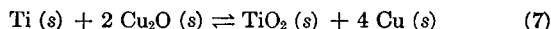
$$NiO\ (s) + TiO_2\ (s) \rightleftharpoons NiTiO_3\ (s) \tag{5}$$

$$2\ NiO\ (s) + TiO_2\ (s) \rightleftharpoons Ni_2TiO_4\ (s) \tag{6}$$

Figure 5. Oxide Films on 70 Ti-Ni at 1 Mm. of Oxygen
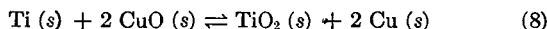for Various Times and Temperatures

Hunter and Bacon (*14*) studied the electrical properties of nickel-titanium alloys and found that alloys containing up to 10% titanium oxidized to a considerable degree when heated to a bright red heat by an electric current. When the wires were cooled, the oxide split off the wire very easily, leaving a fresh surface for further oxidation to occur. This behavior would make the alloys unsuitable as resistance wire material for use at high temperatures.

28 Ti-Cu. Figure 6 shows that cuprous oxide is obtained at 300° and 400° C., while at 500° C. and above rutile forms on the surface. For short oxidation times at 300° and 400° C. a pattern of copper is obtained in addition to cuprous oxide. Previous work (*9*) on the oxidation of copper did not show the metal pattern even in the vacuum of the camera. The presence of titanium appears to have reduced the oxidation rate of copper. Since titanium appears to withstand oxidation better than copper, the addition of small percentages of titanium may be beneficial in those applications where copper and its alloys are used at moderately high temperatures.

The thermodynamic data of Table VI indicate that titanium should reduce the oxides of copper according to the following reactions:

$$Ti\ (s) + 2\ Cu_2O\ (s) \rightleftharpoons TiO_2\ (s) + 4\ Cu\ (s) \tag{7}$$

since $K_R = 10^{+50.2}$ at 300° C. and $10^{+29.6}$ at 700° C.

$$Ti\ (s) + 2\ CuO\ (s) \rightleftharpoons TiO_2\ (s) + 2\ Cu\ (s) \tag{8}$$

since $K_R = 10^{+73.8}$ at 300° C. and $10^{+35.8}$ at 700° C.

The fact that cuprous oxide is obtained below 500° C. may indicate that the rates of formation and diffusion of titanium ions are not sufficiently high for solid phase reactions (*7*) and (*8*) to occur. Oxidation of the alloy is probably occurring by the same mechanism as obtained with copper. Above 500° C. titanium ions are forming and diffusing to the surface, so that any cuprous oxide which forms is reduced and rutile is observed. The results give no indications that solid phase reactions which form titanates occur up to 700° C.

20 Zr-Cu. Figure 7 shows that only oxides of copper are obtained over the complete time-temperature range. Below

500° C. cuprous oxide is the only oxide observed, while at 500° C. it occurs for short oxidation times, followed by the appearance of cupric oxide as the film gets thicker. Above 500° C. cupric oxide occurs alone in the outer surface of the oxide layer.

An earlier study of the oxides formed on copper (*9*) showed only the presence of cuprous oxide in the temperature range 100° to 500° C. This is in agreement with the thermodynamic data (Table VI) which show that cupric oxide should not form on the surface in the temperature range 300° to 700° C. The following solid phase reaction should occur if oxidation is proceeding by the outward movement of copper ions:

$$Cu\ (s) + CuO\ (s) \rightleftharpoons Cu_2O\ (s) \tag{9}$$
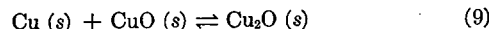
where $K_R = 10^{+2.4}$ at 300° C. and $10^{+1.7}$ at 700° C. However, it is known that cupric oxide does exist in the outer surface of the oxide layer on copper when oxidation occurs above 500° C. This can occur if copper ions do not form and diffuse to the surface, so that Reaction 9 cannot occur. Under these circumstances the following reaction becomes important:

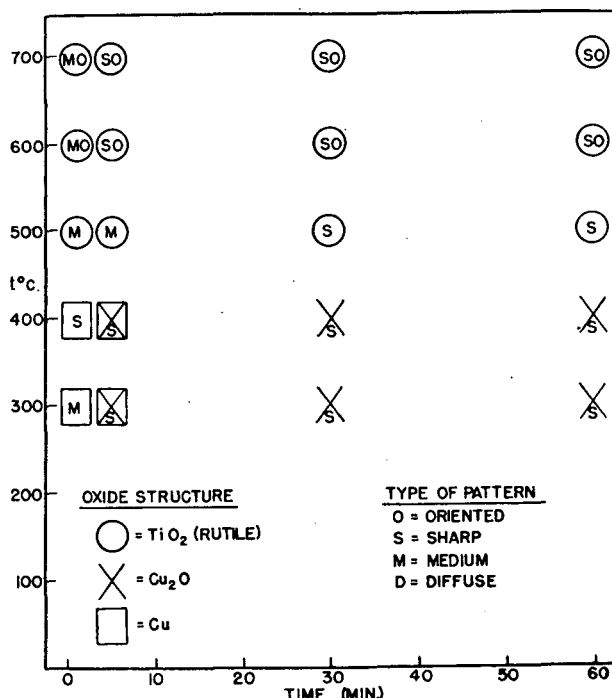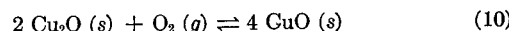$$2\ Cu_2O\ (s) + O_2\ (g) \rightleftharpoons 4\ CuO\ (s) \tag{10}$$

Figure 6. Oxide Films on 28 Ti-Cu at 1 Mm. of Oxygen
for Various Times and Temperatures

If the above explanation for the oxidation mechanism of copper is correct, the addition of an alloying metal to copper which suppresses the formation and diffusion of copper ions should decrease the oxidation rate.

In the case of the 20 Zr-Cu alloy the addition of zirconium appears to have reduced the rate with which copper ions reach the surface, since cupric oxide is observed at 500° C. The authors' results cannot determine whether the binding forces hold copper in the alloy lattice more strongly than in pure copper, which would determine the rate of formation of copper ions, or whether the presence of zirconium oxide in contact with the metal surface offers greater resistance to the passage of copper ions toward the surface. The results do indicate that the alloy may oxidize less readily than pure copper and that the rates of formation and diffusion of zirconium ions are less than those of copper ions. If zirconium ions did diffuse to the surface, copper oxides would not
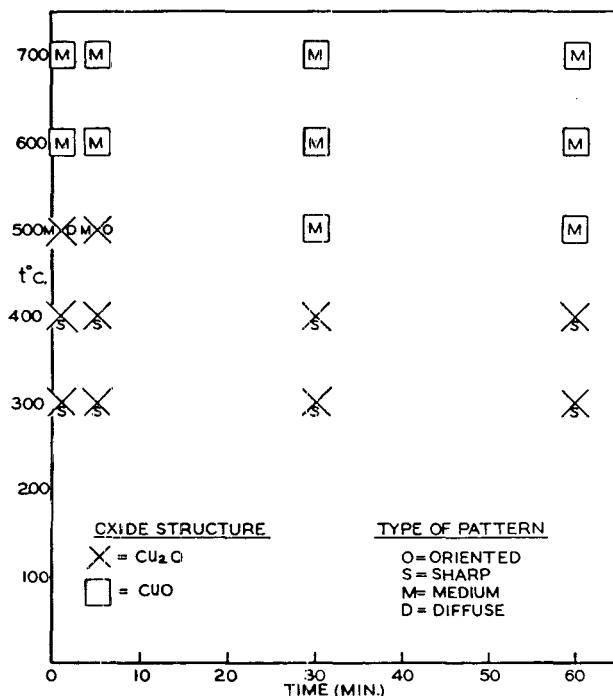
Figure 7. Oxide Films on 20 Zr-Cu at 1 Mm. of Oxygen for Various Times and Temperatures

be observed, since solid phase reactions would result in the reduction of the copper oxides and the formation of zirconium oxide.

60 Zr-Co. Figure 8 shows that cobalto-cobaltic oxide (Co_3O_4) is the only oxide observed over the complete time-temperature range. An earlier study of the oxidation of cobalt (8) showed that a mixture of cobaltous oxide and cobalto-cobaltic oxide is obtained below 500° C., while cobaltous oxide occurred alone above that temperature. In the temperature range 300° to 700° C. cobaltous oxide should be the only oxide observed, since the following reaction should occur:

$$Co\ (s)\ +\ Co_3O_4\ (s)\ \rightleftharpoons\ 4\ CoO\ (s) \tag{11}$$

where $K_R = 10^{+12.9}$ at 300° C. and $10^{+7.5}$ at 700° C. Since cobalto-cobaltic oxide is observed on cobalt below 500° C., the rates of formation and diffusion of cobalt ions must not be high enough to cause Reaction 11 to occur. The following reaction is probably important in determining the oxide which forms:

$$3\ CoO\ (s)\ +\ ^1\!/_2\ O_2\ (g)\ \rightleftharpoons\ Co_3O_4\ (s) \tag{12}$$
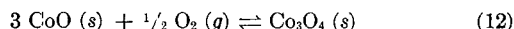
Above 500° C. sufficient cobalt ions reach the surface so that cobaltous oxide forms directly or a solid phase reaction according to Reaction 11 occurs.

On 60 Zr-Co the rates of formation and diffusion of cobalt ions appear to be lower than on cobalt metal, since cobalto-cobaltic oxide is observed up to 700° C. Zirconium ions are not reaching the surface, since zirconium oxide is not observed. The addition of cobalt to zirconium also appears to have reduced the oxidation rate of zirconium, since the 60 Zr-Co alloy could be oxidized safely at 700° C. while zirconium could not. The fact that the oxide film could not be removed from the alloy indicates that a stratification of oxides may have occurred with zirconium oxide in contact with the substrate and cobalto-cobaltic oxide on the outside.

70 Zr-Ni. Figure 9 shows only the presence of nickel oxide on the surface of this alloy. This is not in agreement with thermodynamic data (Table VI), since the following solid phase reaction should occur:

$$Zr\ (s)\ +\ 2\ NiO\ (s)\ \rightleftharpoons\ ZrO_2\ (s)\ +\ 2\ Ni\ (s) \tag{13}$$
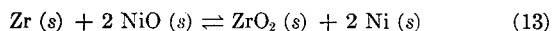
where $K_R = 10^{+51.7}$ at 300° C. and $10^{+31.9}$ at 700° C. This solid phase reaction does not occur in the outer surface of the oxide layer, indicating that zirconium ions are not forming and diffusing to the surface. These results show that nickel ions have higher rates of formation and diffusion than zirconium ions in the temperature range 300° to 700° C.

CONCLUSIONS

The rutile modification of titanium dioxide is the oxide which forms when titanium is oxidized in the temperature range 300° to
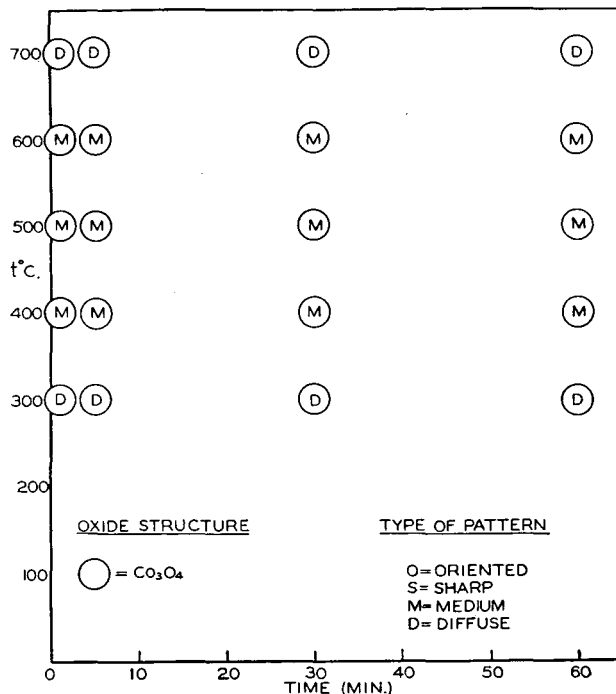

Figure 8. Oxide Films on 60 Zr-Co at 1 Mm. of Oxygen for Various Times and Temperatures
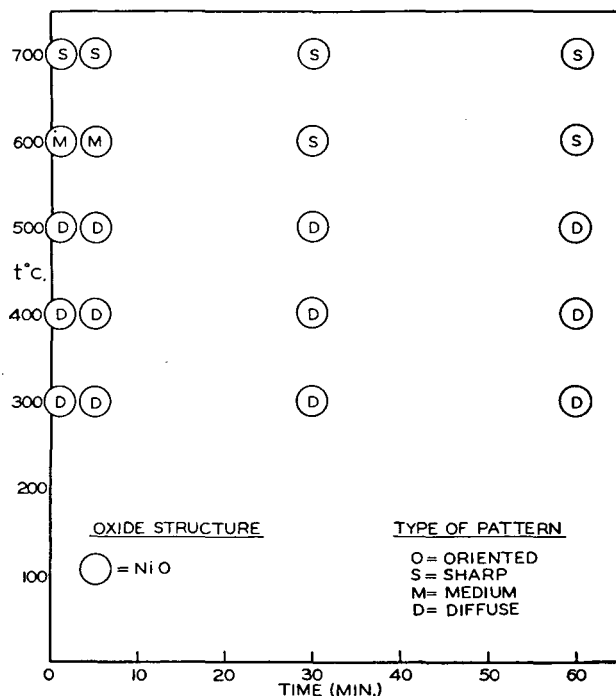

Figure 9. Oxide Films on 70 Zr-Ni at 1 Mm. of Oxygen for Various Times and Temperatures

700° C. Titanium does not appear to oxidize very rapidly below 700° C. when the metal is in the rod form. The oxide film which forms may be removed without much difficulty. Solid phase reactions between titanium metal and the oxide do not occur below 700° C. when the oxide is in the form of a thin film.

The oxidation of zirconium shows only the presence of the monoclinic modification of zirconium dioxide. The character of the reflection patterns and the appearance of the oxidized surfaces indicate that solubility of oxygen or oxide in the metal lattice may occur.

The alloys 50 Ti-Ni and 70 Ti-Ni displayed fairly good oxidation resistance up to 700° C., the 50 Ti-Ni alloy being the better of the two. No oxides of nickel are observed, indicating that titanium ion has greater rates of formation and diffusion than nickel ion or that solid phase reactions between titanium and nickel oxide occur over the temperature range studied. There is no indication that solid phase reactions of the type which form meta- or orthotitanates occur on these alloys.

The oxidation of 28 Ti-Cu shows that below 500° C. copper ions have a greater tendency to get to the surface, while above 500° C. titanium ions diffuse to the surface to form rutile. This suggests that a study of copper-nickel alloys would be interesting since titanium ions diffuse more easily than nickel ions up to 700° C. but less easily than copper ions below 500° C. Since titanium appears to be more oxidation-resistant than copper, the addition of titanium to copper and copper alloys may be beneficial where uses at elevated temperatures are required.

The zirconium alloys do not show the presence of zirconium dioxide up to 700° C. Thermodynamic data indicate that zirconium dioxide should be observed. One explanation for this may be that the rates of formation and diffusion of zirconium ions may be much lower than those of cobalt, copper, and nickel ions.

A comparison of the oxides formed on all the alloys indicates that titanium ions may have higher rates of formation and diffusion than zirconium ions.

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Thorium in Monazite Sand

Separation and Determination by Precipitation from Homogeneous Solution

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A new method based on precipitation from homogeneous solution and devised for the separation and determination of thorium in monazite sand, consists of three steps: decomposition of monazite sand with perchloric acid, separation of thorium and the rare earths by the hydrolysis of methyl oxalate in acid solution, and separation of thorium from the rare earths by the hydrolysis of urea in the presence of formic acid. The faster decomposition of monazite sand with perchloric acid and the formation of dense, easily filtered and washed precipitates result in a more accurate and rapid method.

IN THE method of precipitation from homogeneous solution, a substance is made to undergo a reaction in such a manner that it produces, or results in, the formation of the precipitant homogeneously throughout the entire solution. This method of precipitation has been successfully employed by Willard and co-workers (15, 17-20) to produce dense, easily filtered and washed precipitates which carry down few impurities. These workers hydrolyzed urea to produce a gradual and uniform increase in pH in effecting the separation of gallium, aluminum, and iron as basic salts, and they hydrolyzed triethyl phosphate for the fractional separation of hafnium and zirconium phosphates.

This paper extends the work to the formation of ions other than hydroxyl and phosphate. The hydrolysis of methyl oxalate is successfully employed to separate thorium and the rare earths from their accompanying constituents in monazite sand; urea is

then employed in the determination of thorium in the presence of the rare earths.

A new method has been devised for the determination of thorium in monazite sand by incorporating the two precipitations from homogeneous solution mentioned above. This new method also includes a very rapid plan for effecting decomposition of monazite sand.

The determination of thorium generally follows one of two general schemes. The sand is first decomposed by a long (5 to 8 hours) treatment with sulfuric acid (7). Not only is this method time-consuming but it is made more difficult because of the necessity of extracting the sulfates with ice-cold water in order to prevent the formation of insoluble thorium and rare earth sulfates.

By one general scheme, thorium, lanthanum, cerium, praseodymium, neodymium, and traces of the other rare earths can be separated from the sulfuric acid solution of the monazite sand by

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oxalic acid, and thorium subsequently separated from these constituents by methods that employ such reagents as sebacic acid (16), fumaric acid (9), m-nitrobenzoic acid (11), phenylarsonic acid (12), quinaldic acid (6), 8-hydroxyquinoline (1), sodium thiosulfate (14), potassium trinitride (4, 5), hexamine (8), and hydrogen peroxide (21, 22).

By the other general scheme, the direct separation of thorium and the small quantities of titanium, zirconium, and quadrivalent cerium from the other constituents can be effected by the use of potassium iodate (10), sodium pyrophosphate (3), or sodium hypophosphate (13). Oxalic acid is then used to separate thorium from the quadrivalent ions mentioned.

The use of either of these general schemes, or any intercombination of methods, results in the type of precipitate with which is associated one or more of the following: a long digestion period to improve the precipitate, difficulty in washing the precipitate free of interfering ions, difficulty in converting the insoluble thorium compounds into soluble compounds for reprecipitation purposes, or reprecipitation in order to effect more complete separation.

MATERIALS USED

Preparation of Pure Thorium Perchlorate Solutions. Approximately 25 grams of c.p. thorium nitrate and 100 grams of c.p. ammonium chloride were dissolved in 2000 ml. of water slightly acidified with nitric acid and then 50 grams of c.p. urea were added. The solution was gently boiled until a pH of 6.0 was reached. This first precipitate was filtered and washed with hot 2% ammonium nitrate solution adjusted to pH of 6.0.

The precipitate was dissolved with hot 2 N hydrochloric acid, the resulting solution being diluted to 2000 ml. Then 100 grams of ammonium chloride were added and this time the thorium was precipitated by the hexamine method (8) until a pH of 6.0 was reached. The precipitate was filtered, washed, and redissolved as before.

From this solution the thorium was precipitated with oxalic acid. This precipitate was allowed to stand overnight on the hot plate, then filtered and washed with hot 2% oxalic acid solution to which hydrochloric acid had been added to adjust the pH to 0.5.

The precipitate was dissolved in nitric-perchloric acid mixture, warmed to fumes of perchloric acid, reprecipitated as the oxalate, and washed as before.

The final precipitate was ignited at 300° C. for 24 hours. Solutions of thorium perchlorate of approximately the strength desired were made by dissolving the ignited precipitate in nitric-perchloric acid mixture, evaporating to fumes of perchloric acid, diluting, and finally determining the thorium content by the sebacic acid method or by precipitation with oxalic acid.

The thorium solution thus prepared was free of iron, titanium, aluminum, phosphorus, and the rare earths.

Preparation of Rare Earth Perchlorate Solutions. The rare earth salts used were c.p. products. They were further purified, being made thorium-free by the addition of hexamine to a pH of 6.0, followed by filtration. The rare earths were then precipitated with oxalic acid, and the precipitate was filtered, washed, and dissolved in nitric-perchloric acid mixture as in the purification of thorium.

The rare earth perchlorates thus prepared were those of lanthanum, cerium, praseodymium, neodymium, yttrium, and gadolinium.

Other Materials. Urea, ammonium chloride, formic acid (87 to 90%), perchloric acid (70%), and other materials used were c.p. quality. Methyl oxalate and hydrazine dihydrochloride were Eastman products.

DECOMPOSITION OF MONAZITE

It was found that monazite sand dissolved rapidly in boiling 70% perchloric acid. The formation of a yellow precipitate, apparently ceric phosphate, began soon after boiling.

When the solution was cooled and diluted with water, a yellow gelatinous precipitate of basic ceric phosphate was formed.

The slow addition of hydrogen peroxide (3%), with the solution being warmed and agitated all during this addition, effects reduction of the quadrivalent cerium and results in clarification of the mixture except for a small unattackable residue which does not contain thorium. The complete removal of the excess hydro-

gen peroxide is extremely difficult and the substitution of hydrazine dihydrochloride as the reducing agent was found very satisfactory.

SEPARATION OF THORIUM AND RARE EARTHS WITH METHYL OXALATE

The method of separating thorium and the rare earths by the addition of oxalic acid necessarily results in the occlusion of considerable phosphate. The size of a monazite sample normally taken for analysis is 1 to 5 grams, of which 60% represents thorium and rare earth oxides and 30% is phosphorus pentoxide. Upon the addition of oxalic acid, a gummy precipitate is initially formed and a 15-hour digestion is necessary in order to remove a considerable fraction of the initially occluded phosphate.

It appeared evident from early experiments that methyl oxalate hydrolyzed fairly readily in acid solution and that its use resulted in marked improvement in the characteristics of the precipitate.

Complete precipitation of thorium as the oxalate can be effected in a solution containing no more than 4 ml. of concentrated hydrochloric acid per 100 ml. (7). This is approximately a 0.5 N solution; the oxalic acid concentration is usually also made 0.5 N.

When crystals of methyl oxalate were added to a solution approximately 0.5 N in perchloric acid and the solution was gently warmed and stirred, the crystals slowly dissolved and within a few minutes precipitation occurred due to the hydrolysis of methyl oxalate. After 30 minutes of warming, at approximately 85° C., and with stirring, the oxalates of thorium and the rare earths were found to be much larger in size than those obtained by means of an ordinary oxalic acid precipitation.

In order to prevent the formation of an initial gelatinous precipitate, the solution had to be very acid and to ensure complete precipitation of the thorium, it became necessary to employ a two-stage precipitation. First, a major portion of the thorium was precipitated by the hydrolysis of methyl oxalate in a very small volume of very acid solution and an oxalic acid solution was then added to precipitate any traces of thorium which remained in solution. The final volume was such that the solution was approximately 0.5 N in perchloric acid.

Even with this improved precipitation procedure, a small amount of phosphate is occluded. With a monazite sample weighing 1.25 grams and containing approximately 0.4 gram of phosphorus pentoxide, there remained about 0.0005 gram of the latter.

Since reprecipitation is necessary to remove this residual phosphate, it was accomplished by decomposing both the filter paper and the oxalates by use of a nitric-perchloric acid mixture and employing the hydrolysis of methyl oxalate as before. This use

Table I.   Comparison of Three Methods of Precipitating Thorium

No.	Sebacic acid method	Hexamine method	Urea method
	Thorium Oxide Found		
	Gram	Gram	Gram
1	0.0899	0.0899	0.0899
2	0.0901	0.0899	0.0897
3	....	....	0.0901
4	....	....	0.0899
5	....	....	0.0901
	Av. 0.0900	0.0899	0.0899

Table II.   Silica Content of Thorium Precipitates

(ThO₂ taken = 0.1109 gram)

	Single Precipitation		Double Precipitation	
	No. 1	No. 2	No. 3	No. 4
ThO₂ and SiO₂ found, gram	0.1117	0.1117	0.1114	0.1113
SiO₂ found, gram	0.0008	0.0008	0.0005	0.0005
ThO₂ found, gram	0.1109	0.1109	0.1109	0.1108

Table III. Separation of Thorium and Cerium by Urea-Formate Method

(ThO₂ taken = 0.1109 gram. CeO₂ taken = 0.5025 gram)

	Single Precipitation			Double Precipitation		
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Weight of ppt. found, gram	0.1127	0.1125	0.1127	0.1114	0.1113	0.1113
SiO₂ found, gram	......	......	......	0.0005	0.0005	0.0002
ThO₂ found, gram	......	......	......	0.1109	0.1108	0.1111
Difference, gram	+0.0018	+0.0016	+0.0018	±0.0000	−0.0001	+0.0002

Table IV. Separation of Thorium from Rare Earths with Double Precipitation by Urea-Formate Method

(Rare earths taken = 0.2370 gram La₂O₃, 0.5025 gram CeO₂, 0.0886 gram Pr₆O₁₁, 0.1830 gram Nd₂O₃, 0.0145 gram Y₂O₃, 0.0010 gram Gd₂O₃)

No.	ThO₂ Taken Gram	Ppt. Found Gram	SiO₂ Found Mg.	ThO₂ Found Gram	Diff. Mg.
1	0.1109	0.1109	0.9	0.1110	+0.1
2	0.1109	0.1122	1.1	0.1111	+0.2
3	0.1109	0.1121	1.1	0.1110	+0.1
4	0.0555	0.0559	0.5	0.0554	+0.1
5	0.0555	0.0563	0.6	0.0557	+0.2

of a nitric-perchloric acid mixture resulted in a more rapid decomposition than can be obtained by the conventional methods, which either use nitric acid alone or employ an ignition followed by solution of the oxides thus formed in hydrochloric acid.

PRECIPITATION OF BASIC THORIUM FORMATE BY HYDROLYSIS OF UREA

Preliminary Investigation. In previous work (15, 17, 19, 20) it had been found that the presence of certain anions, particularly sulfate, succinate, and formate, contributed to the formation of dense precipitates. The use of sulfate is precluded in the precipitation of thorium because of the formation of the slightly soluble sulfates of both thorium and the rare earths. Succinate ion was found unsuitable but the use of formate resulted in the formation of a precipitate which was dense, readily filterable, and easily washed. The use of acetate or propionate ion did not produce so dense a precipitate even if the precipitation was carried out over a longer interval of time than with formate.

Since ammonium salts allowed better control of the final pH, their employment was advisable.

pH of Initial Precipitation. Britton (2) states that thorium hydroxide precipitates at a pH of 3.5 Because this value is dependent on several factors, it was necessary to determine the pH at which thorium began to precipitate from solution containing substances as indicated in the subsequent directions for the determination of thorium in monazite sand. It was found that the opalescence due to precipitation of a basic salt appeared at a pH of 4.45 to 4.50.

pH of Quantitative Precipitation. Basic thorium formate is completely precipitated at a pH of approximately 5.3 by the urea-formate method.

Adherence of Film to Beaker Walls. Some basic thorium formate deposits on the beaker walls and on the stirring rods in the form of a thin, tenacious, somewhat transparent film.

On the inside surfaces of two beakers in which precipitations were carried out and where the glass surfaces were so thoroughly cleaned with a policeman that no visible traces of a precipitate or film appeared, there were found 2.6 and 1.8 mg. of thorium oxide. Removal of these films were effected by adding 10 ml. of dilute hydrochloric acid, covering the beaker with a watch glass, and gently refluxing the acid for 5 to 10 minutes.

Comparison of Urea, Sebacic Acid, and Hexamine Methods for Precipitation of Thorium. In Table I are given the results of a comparison of the amounts of thorium oxide obtained by the urea, the sebacic acid, and the hexamine methods.

Silica Content of Basic Thorium Formate. In Table I the variation of 4 parts per 1000 in two of the urea values was subsequently traced to the presence of silica entrained in the thorium

precipitate. This silica obviously is transmitted from the glassware, probably from the adherent film.

Table II furnishes data on the amount of silica brought down with the thorium. For some of the experiments in Table II, the precipitate was redissolved and again precipitated. This scavenger effect of the thorium precipitate for silica made it necessary to volatilize silica before weighing all precipitates.

SEPARATION OF THORIUM FROM CERIUM

Reduction of Quadrivalent Cerium. Of the reducing agents which might be employed for the reduction of quadrivalent cerium in the urea-formate method, hydrogen iodide, hydroxylamine, hydrazine, and hydroquinone appeared to possess the necessary qualifications.

Hydrogen iodide effected the best separation, as was indicated by experiments in which 0.1109 gram of thorium oxide was precipitated in the presence of 0.5025 gram of ceric oxide. The excess weight of the precipitates when hydrogen iodide was used was approximately 1.7 mg.; with hydroxylamine, 4.1 mg.; with hydrazine, 3.0 mg.; and with hydroquinone, 4.8 mg.

Double Precipitation of Thorium. A single precipitation did not effect complete separation of thorium from cerium. This necessitated dissolving the precipitate from the filter paper with hot 2 N hydrochloric acid, then reprecipitating in the usual manner. In Table III are shown the results obtained by both the single and double precipitations.

SEPARATION OF THORIUM FROM LANTHANUM, PRASEODYMIUM, NEODYMIUM, YTTRIUM, AND GADOLINIUM

Single Precipitation. In three experiments in which was attempted the separation of 0.1109 gram of thorium oxide from 0.2370 gram of lanthanum oxide, 0.0886 gram of praseodymium oxide, 0.1830 gram of neodymium oxide, 0.0145 gram of yttrium oxide, and 0.0010 gram of gadolinium oxide, there were obtained precipitates which were from 2.3 to 2.4 mg. too heavy.

SEPARATION OF THORIUM FROM LANTHANUM, CERIUM, PRASEODYMIUM, NEODYMIUM, YTTRIUM, AND GADOLINIUM BY DOUBLE PRECIPITATION

In Table IV are given the results of the separation of thorium from the rare earths by double precipitation. The double precipitation effected a complete separation of thorium from the rare earths.

DETERMINATION OF THORIUM IN MONAZITE SAND

Decomposition of Monazite Sand with Perchloric Acid. Weigh 50 grams of monazite sand into a large-mouthed 1000-ml. Erlenmeyer flask provided with a pouring lip to facilitate the subsequent transfer of the flask contents. Add 200 ml. of 70% perchloric acid, bring to a boil, and continue vigorous boiling for 1 to 1.25 hours. Do not cover the flask, inasmuch as the return of traces of water to the solution reduces the solvent activity of the perchloric acid.

Cool the contents of the flask somewhat, add 50 ml. of 70% perchloric acid, then add 300 ml. of water slowly and with considerable agitation of the flask contents. Now slowly add, with vigorous shaking of the solution, 18 grams of hydrazine dihydrochloride crystals. Warm gently for one hour to remove gaseous decomposition products. The solution will clarify considerably but there will remain a solid residue consisting of zircon, quartz, rutile, ilmenite, and dehydrated silica.

Cool the flask with tap water, then add 3 grams of purified diatomaceous earth (Filter-cel). Agitate the solution thoroughly in order to distribute the diatomaceous earth well throughout the solution. Filter through a medium-porosity 15-cm. filter paper, using a small perforated platinum cone for support. Wash the residue thoroughly with 1 to 3 perchloric acid. Remove the filter paper and residue to a small beaker, add a few milliliters of 1 to 3 perchloric acid, macerate the filter paper with a stirring

Table V. Thorium Dioxide Found in Brazilian Monazite by Urea-Formate and Iodate Methods

No.	Iodate Method	Urea-Formate Method	
		N₂H₄ reduction	H₂O₂ reduction
	%	%	%
1	6.23	6.42	6.42
2	6.25	6.34	6.42
3	6.26	6.35	6.35

rod, and decant through an 11-cm. medium-porosity filter. Wash the residue in the beaker several times in this same manner. Dilute the combined filtrates to 1000 ml. with 1 to 3 perchloric acid.

Precipitation of Thorium with the Rare Earth Oxalates with Methyl Oxalate. Pipet 25 ml. of the perchloric acid solution of monazite sand into a 600-ml. beaker and add concentrated, silica-free ammonium hydroxide dropwise by medicine dropper, with complete mixing after each drop, to the appearance of a permanent turbidity. Then add 10 ml. of concentrated hydrochloric acid and allow the solution to stand for 5 minutes with occasional mixing of the contents.

Add 100 ml. of water, followed by 6 grams of methyl oxalate. Use slow mechanical stirring and gently warm the contents (70° to 85° C.) for 30 minutes. The methyl oxalate will dissolve, the solution becoming clear, and within a few minutes after clarification precipitation will occur.

After the 30-minute warming period, add a hot solution of 8 grams of oxalic acid in 280 ml. of water, and stir for an additional 30 minutes, keeping the solution warm.

Cool the solution to room temperature, then filter the precipitate through an 11-cm. medium-porosity ashless filter, and wash ten times with a 2% oxalic acid solution containing 40 ml. of concentrated hydrochloric acid per liter. Washing by decantation is very easy and is recommended.

Transfer the filter and precipitate to the 600-ml. beaker containing the oxalates, add 20 ml. of concentrated nitric acid, followed by 5 ml. of 70% perchloric acid, then warm gently until fumes of perchloric acid appear. Cool the solution.

Add 200 ml. of water, followed by 6 grams of methyl oxalate. Warm the solution with constant stirring for 30 minutes as in the initial precipitation. Add a hot solution of 8 grams of oxalic acid in 200 ml. of water and continue the stirring and warming for an additional half hour.

Cool the solution to room temperature, filter, and wash as in the initial procedure. Five washings by decantation are sufficient.

Decompose the filter paper and oxalates by evaporating with 20 ml. of concentrated nitric acid and 10 ml. of 70% perchloric acid to fumes of the latter. The solution is now free of even a trace of phosphate, and is ready for the separation of thorium from the rare earths.

Separation of Thorium from Rare Earths by Urea-Formate Method. Cool the solution of thorium and rare earth perchlorates obtained from the methyl oxalate precipitation to room temperature. Add 1 gram of potassium iodide in 25 ml. of water, followed by 8 grams of urea, 10 grams of ammonium chloride, and 3 ml. of formic acid (87 to 90%), the last three reagents being dissolved in about 150 ml. of water. The solution containing the urea, ammonium chloride, and formic acid should be filtered before it is added to the thorium solution.

Dilute the solution thus obtained to approximately 350 ml. and using ammonium hydroxide freshly prepared from gaseous ammonia (or any silica-free ammonium hydroxide), adjust the pH to 4.45 ± 0.02, preferably by the following procedure: Calibrate the external glass electrode of a pH meter against a potassium acid phthalate buffer of a pH of 4.00. Then adjust the pH of the thorium solution to 4.45 ± 0.02. Adjust the final volume to approximately 450 ml.

Using a stirring rod with about a 1-mm. indentation in one end made with a carpet tack, bring the solution to a boil, and adjust the heat so that a steady stream of bubbles just issues from the stirring rod indentation. Boil gently for 95 to 97 minutes after appearance of the opalescence.

The final pH should be 5.4 to 6.2. If less than 5.4, incomplete precipitation occurs and it will be necessary to boil the solution a little longer. If more than 6.2, some of the rare earths may precipitate, but this is not generally serious, since they will be removed by the double precipitation. In over 90% of the precipitations, this final pH will fall within the limits, 5.5 to 5.9.

Filter, and wash ten times, using a hot solution containing 20 grams of ammonium nitrate and 8 ml. of formic acid (87 to 90%) per liter; the pH of the wash solution should be adjusted to 5.6 with ammonium hydroxide.

Remove most of the thorium precipitate remaining on the beaker walls with a single policeman treatment. Place this beaker with stirring rod under the funnel and dissolve the precipitate

from the filter with hot 2 N hydrochloric acid. Wash the filter thoroughly with the acid wash.

Now add as before, 1 gram of potassium iodide, then 8 grams of urea, 10 grams of ammonium chloride, and 3 ml. of formic acid. Adjust the pH to 4.45 ± 0.02, and boil 95 to 97 minutes until the final pH is 5.4 to 6.0. Filter, then wash ten times as before.

Next, remove most of the thorium precipitate from the beaker walls by a single policeman treatment and pour onto the filter. Add to the beaker 5 ml. of concentrated hydrochloric acid and 5 ml. of water, insert the stirring rod, cover with the watch glass, and reflux gently for 10 minutes. Wash down the watch glass, beaker walls, and stirring rod with distilled water, then add ammonium hydroxide dropwise until the solution turns purple to bromocresol purple indicator. Warm gently for 1 to 2 minutes.

Filter the few milligrams of gelatinous precipitate through the filter containing the basic thorium formate. Wash five times. Ignite in a platinum crucible for 2 hours at 950° C. Remove silica by treatment with hydrofluoric and sulfuric acids, then ignite for 2 hours at 950° C. or to constant weight.

COMPARISON OF UREA-FORMATE AND IODATE METHODS FOR DETERMINATION OF THORIUM

In Table V are shown the results obtained in determining the thorium oxide content of a Brazilian monazite by the iodate and the urea-formate methods. Results are also furnished for a determination where the somewhat troublesome hydrogen peroxide reduction of the cerium was employed. In this latter case it was necessary to remove 25-ml. aliquots of the monazite solution as soon as it was diluted to prevent the error of a volume change resulting from escaping oxygen.

The results in Table V indicated a wide discrepancy between the two methods and necessitated a critical evaluation of the iodate method (10).

Two sources of error were found in the iodate method: the postprecipitation of thorium iodate, and the faulty technique of using the original filter paper through which the thorium iodate is filtered for the final ignition of thorium oxalate. There appears to be a compensation of errors whereby the loss of thorium due to postprecipitation of thorium iodate is offset by the gain in weight due to silica entrained on the filter. This silica appears as colloidal material in the monazite solution and is not removed by the first filtration just prior to dilution to volume.

When the precipitates of thorium oxide obtained by the iodate method were analyzed for silica, they were found to contain 1.1, 2.9, and 2.4 mg. and the thorium oxide percentages for the iodate method as given in Table V became 6.19, 6.14, and 6.16%, respectively.

Table VI. Thorium Oxide Found in Brazilian Monazite by Urea-Formate and Modified Hexamine Methods

No.	Urea-Formate Method	Hexamine Method
	%	%
1	6.42	6.36
2	6.34	6.42
3	6.35	6.39
Av.	6.37	6.39

COMPARISON OF UREA-FORMATE AND MODIFIED HEXAMINE METHODS

In Table VI are shown the results comparing the urea-formate with the modified hexamine method. The modification merely consisted in determining thorium by the hexamine method in the mixture of oxalates obtained from the perchloric acid–methyl oxalate procedure. In the original method monazite is decomposed by sulfuric acid and the oxalates are obtained by precipitation with oxalic acid. The results of Table VI indicate excellent agreement between the two methods.

It was interesting to compare the silica content in the thorium oxide precipitates. For the urea-formate method, samples 1, 2, and 3 contained, respectively, 0.6, 0.7, and 0.8 mg., whereas each of the precipitates obtained by the hexamine method contained

less than 0.1 mg. This verified the "silica-scavenger" properties of the basic thorium formate obtained by the urea method.

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Acidimetric Determination of Aluminum

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A method for determining aluminum is described in which a caustic solution of aluminate is titrated with hydrochloric acid from pH of approximately 11 to 3. The point at which the free caustic is neutralized and the reaction with aluminate starts (about pH 11) is identified by potentiometric measurements. The end point at which the conversion of the aluminum to the chloride is complete is identified visually and indirectly by an application of Scott's method with potassium fluoride. The accuracy and precision of the method are discussed, as is the effect of interfering substances. Titration curves are presented that show the variation of pH as soluti ons containing aluminum are titrated with acid or base.

THE strong hydrolysis of salts such as aluminum chloride imparts to them weakly acid properties. This suggests the possibility of determining aluminum in solution by titrating with a base. Many methods have been proposed for making the analysis in this manner.

Scott (*6*), in a modification of Craig's (*2*) method, describes a procedure for determining aluminum in which two portions of the sample are titrated. One aliquot of the solution of aluminum in excess free acid is titrated with sodium hydroxide to the phenolphthalein end point. This results in neutralization of the excess free acid and precipitation of aluminum as the hydroxide and permits calculation of the total acid content of the solution. Another aliquot of equal size is treated with an excess of potassium fluoride to precipitate potassium cryolite:

$$AlCl_3 + 6KF \rightarrow K_3AlF_6 \downarrow + 3KCl$$

Subsequent titration of the resulting suspension with sodium hydroxide to the phenolphthalein end point results only in neutralization of the free acid. This permits calculation of the free acid content of the solution. The difference between the two titration values is thus equivalent to the aluminum.

Both potassium and sodium cryolite are appreciably soluble precipitates, the former more so than the latter. The potassium salt is employed, however, because the high solubility of potassium fluoride permits addition of a great excess of the reagent to drive the reaction to completion. If the cryolite is precipitated in a strongly acid solution, the precipitate carries down considerable free acid that will not be subject to the subsequent titration. For this reason Scott's procedure should be modified by carrying the titration for free acid nearly to the point of precipitation of aluminum hydroxide before addition of fluoride. This same observation has recently been made by Graham (*4*). The end point in the titration for total acid leaves much to be desired. It is subject to error due to coprecipitation and to the nature and concentration of various salts present in solution.

Snyder (*7*) proposes the determination of aluminum by neutralization of an acidified aluminum tartrate solution with barium hydroxide to the phenolphthalein end point. The solution is then treated with neutral potassium fluoride solution to precipitate potassium cryolite. The caustic liberated by the conversion of the basic aluminum tartrate to cryolite is then titrated with standard acid. Snyder states that sodium hydroxide cannot be used for the initial neutralization if satisfactory

results are to be obtained. Hale (*5*) has more recently reported that lithium hydroxide may be employed instead of barium hydroxide to effect the neutralization. The author obtained poor results when using sodium hydroxide alone, but acceptable results if barium chloride was first added. The presence of barium was found to affect the nature of the soluble aluminum tartrate complex. The procedure is empirical and the aluminum factor for the standard acid must be found by standardization against a solution of known aluminum content. One cause of this is coprecipitation of some liberated sodium hydroxide with the cryolite. Thus, if potassium fluoride is added to a caustic aluminate solution—either in the presence or absence of tartrate— the subsequent total titration to phenolphthalein will be considerably less than theoretical. This is comparable to the occlusion of acid by cryolite that has been precipitated in acid solution.

The direct determination of aluminum by sodium hydroxide titration has been proposed by the Dow Chemical Co. (*3*) and the A.S.T.M. (*1*). The acidified sample solution is treated with ammonium chloride and the free acid is then neutralized with sodium hydroxide to a potentiometric end point. This is followed by heating the solution and titrating the aluminum with standard sodium hydroxide to a second potentiometric end point corresponding to complete formation of basic aluminum chloride (*8*).

TITRATION OF ALUMINUM WITH SODIUM HYDROXIDE

In the titration of a hydrochloric acid solution of aluminum chloride, the point of neutralization of the free acid is recognized from pH measurements as a break in the titration curve. This point also corresponds to the beginning of the precipitation of aluminum hydroxide. The analytical application of this end point is limited by two factors. First, equilibrium is reached slowly as the point is approached because the addition of each drop of sodium hydroxide produces a local formation of precipitate that is only slowly soluble. Secondly, the actual pH of the end point is dependent on the concentration of aluminum chloride. Since the free acid in solution has been completely neutralized, the pH of this equivalence point will be that of a solution of pure aluminum chloride of the concentration present. The equation for hydrolysis indicates that the hydrogen-ion con-

centration is roughly proportional to the square root of the aluminum concentration.

Figure 1 shows neutralization curves for solutions of aluminum chloride in . dilute hydrochloric acid. The volumes of added 1.000 N sodium hydroxide are plotted against the resulting solution pH as determined potentiometrically with a glass electrode. The pH values of the first inflection points in the three curves are 3.5, 3.1, and 2.9 for the correspondingly greater aluminum chloride concentrations. The titration volumes to the indicated points are 0.28, 1.40, and 2.90 ml. for the 5.0-, 25.0-, and 50.0-ml. aliquots, respectively. The quantity of free acid found is thus proportional to the sample size within reasonable limits.
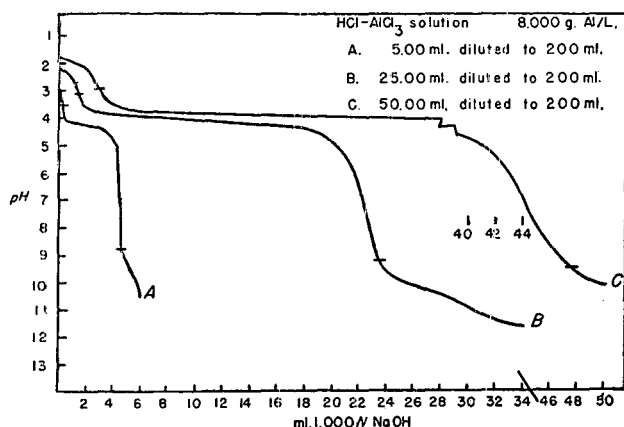
Figure 1. Titration Curves

The second step of the titrations includes the reaction of sodium hydroxide with aluminum to precipitate the hydroxide. The titration volumes to the equivalent points may be calculated from the known weight of aluminum and the above-determined quantity of free acid present in the samples. They are 4.73, 23.65, and 47.39 ml. of the standard sodium hydroxide. These volumes are marked on the curves of Figure 1 and are seen to correspond, respectively, to equivalence point pH values of 8.6, 9.1, and 9.3. The fact that the pH of the stoichiometric end point is greater than that of the inflection point and decreases with the quantity of precipitate present indicates the coprecipitation of aluminum chloride by the solid. The titration at room temperature, as described, is not suitable for analytical determinations.

Attempts to continue the titration and detect the end point at which the aluminum hydroxide dissolved were unsuccessful. In the reaction

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

equilibrium is established so slowly during the dissolution of the precipitate that there is no analytical application.

TITRATION OF ALUMINATE WITH ACID

The curves reproduced in Figure 2 are for titrations of solutions of sodium aluminate in dilute sodium hydroxide with standard hydrochloric acid. The curves are similar to the reverse of the previous ones except that the first inflection point is sharply defined. In practice, during the stepwise addition of acid, equilibrium is rapidly established, so that little time is required to make the several additions of increments of acid and measure the resulting solution pH values. This first inflection point coincides with the start of precipitation of aluminum hydroxide; in fact, with good lighting it may be determined closely by the visible formation of turbidity. It is defined by the complete neutralization of all the free caustic in the sample and is important analytically as the starting point for the acidimetric determination of aluminate.

In the four curves shown, the pH values corresponding to the first inflection are 10.4, 10.8, 11.1, and 11.3. As expected, they differ one from another because the pH of a sodium aluminate solution varies with the concentration; thus the titration cannot be carried to a fixed pH for all samples but must be taken to the inflection as established from the curve. Standardized electrodes are not required because only the volume of the inflection point is required. The volumes of acid represented by the four points are 0.4, 1.8, 4.4, and 6.4 ml. These are closely proportional to the aliquot volumes and are a measure of the free sodium hydroxide content of the samples.

A second observation of interest in the curves of Figure 2 concerns the pH of the suspensions of samples which have been stoichiometrically neutralized to aluminum hydroxide. The titration volumes, as calculated from the above-determined quantities of excess free sodium hydroxide and the known weights of aluminum present in the synthetic samples, are marked. The corresponding pH values are 9.0, 9.1, and 9.5 and are noted not to coincide with the inflection point. They are in remarkable agreement with similar values obtained in the reverse titration as discussed above. The data show that a pH of about 9 is obtained either when an aluminum chloride solution is treated with an equivalent of sodium hydroxide or when a sodium aluminate solution is treated with an equivalent of acid. In neither case does the pH of the equivalence point correspond with that of the inflection point of the titration curve. This indicates that the precipitate retains a small amount of unreacted aluminum chloride—or basic chloride—and the solution a corresponding amount of unreacted free caustic. The situation might be different if sufficient time were allowed for the system to reach permanent equilibrium or if another form of aluminum hydroxide were produced, as, for example, at an elevated temperature.
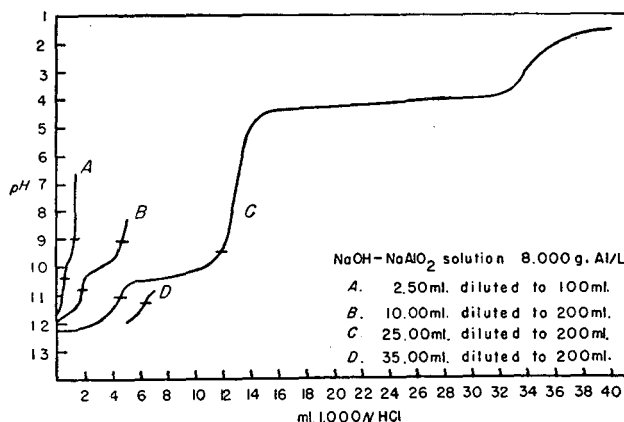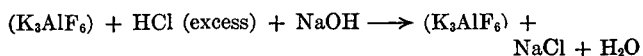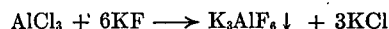

Figure 2. Titration Curves

The third inflection in the curves of Figure 2 represents complete solution of the aluminum hydroxide. It is poorly defined, since the precipitate is only slowly soluble and time is required to obtain the equilibrium pH. The final traces of the precipitate are not readily soluble in the presence of a slight excess of acid; however, the addition of 0.5 to 1 ml. of the potassium fluoride solution will immediately dissolve it.

In practice aluminum in an aluminate solution may be quickly and accurately determined by first neutralizing the excess sodium hydroxide as described. Starting from there, acid is added until a slight excess is present above that required to form aluminum chloride. A solution of neutral potassium fluoride is then added and the small quantity of excess acid determined by back-titration with standard sodium hydroxide to phenolphthalein. The latter step is according to Scott's method as previously discussed. Four moles of acid are thus employed to react with one mole of aluminum. The reactions involved are:

Table I. Acidimetric Determination of Aluminum

(Titration of alkaline NaAlO₂ solution with HCl)

Al Taken	Sample Dilution	Al Found
Gram	Ml.	Gram
0.2000	200	0.2004
0.2000	200	0.2007
0.2000	200	0.2005
0.2000	200	0.2008
0.2000	200	0.2000
0.2000	200	0.2004
0.2000	100	0.2010
0.2000	400	0.2007
0.2800	200	0.2812
0.0800	200	0.0796
0.0200	100	0.0200
0.0200	100	0.0201

$$(NaAlO_2) + NaOH \text{ (free)} + HCl \longrightarrow (NaAlO_2) + NaCl + H_2O$$

$$NaAlO_2 + 4HCl \longrightarrow AlCl_3 + NaCl + 2H_2O$$

$$AlCl_3 + 6KF \longrightarrow K_3AlF_6 \downarrow + 3KCl$$

$$(K_3AlF_6) + HCl \text{ (excess)} + NaOH \longrightarrow (K_3AlF_6) + \\ NaCl + H_2O$$

ACCURACY AND PRECISION

Aliquots of a standard aluminate solution were analyzed according to the method outlined above and described in detail below. The results are summarized in Table I.

Of the twelve determinations, the average deviation from truth is 0.31 part per hundred. There is a definite bias, however, as indicated by the fact that the average result is high by 0.22 part per hundred. Calculation of the coefficient of variation—corrected for bias—shows that two thirds of the results will fall within ±0.28 part per hundred of the mean.

For multiple experiments containing equal quantities of aluminum:

$$\text{Standard deviation} = \sigma = \sqrt{\frac{\Sigma\,(x - \bar{x})^2}{N-1}}$$

$$\text{Coefficient of variation} = \frac{\sigma}{\bar{x}}\,100$$

where x = individual value
  $\bar{x}$ = mean value
  N = number of individual values

For the group of experiments containing unequal quantities of aluminum the percentage error of each result was corrected for the bias, and the resulting relative deviations from the mean were squared, added, and divided by $(N - 1)$. The square root of the quotient is the coefficient of variation.

The data show that a tenfold variation in the quantity of aluminum titrated has no influence on the accuracy; in the last two experiments 0.1 N hydrochloric acid was used as the titrating reagent, in the remainder 1.0 N hydrochloric acid. A fourfold variation in dilution is also without effect.

Another measure of the precision of the method was obtained by analyses of industrial liquors containing sodium hydroxide, carbonate, and aluminate (50 to 100 grams of alumina per liter). Results from duplicate or triplicate aluminum determinations on each of eleven separate liquors had a coefficient of variation of 0.31. Thus, the deviation from the mean was within ±0.31 part per hundred in two thirds of the cases. A similar set of analyses on similar liquors yielded a coefficient of 0.24. In this set, thirteen separate liquors were analyzed in duplicate or triplicate. The standard deviation was found to vary proportionately with the quantity of aluminum titrated, while the coefficient of variation remained essentially constant.

The procedure may be applied in the rapid determination of aluminum in acid solutions. Saturated sodium hydroxide solution is added to the sample until the precipitate that first forms

redissolves as aluminate; this takes place readily, so that not more than several drops of excess sodium hydroxide need be added. The analysis is then completed as described. Results obtained in this manner are on a par with those shown in Table I.

INTERFERENCES

The most common form of interference is by substances that consume acid in the titration. However, the starting point of the titration is at a pH of about 11 (Figure 2) and the final end point, after the addition of potassium fluoride and back-titration, is at a pH of 8.3 corresponding to the phenolphthalein color change. Thus, interference is encountered by substances that consume acid over a net change of the solution pH from 11 to 8.3. Figure 3 gives the titration curves for neutralization of solutions of ammonia and sodium carbonate; the acid consumptions to the phenolphthalein end point (pH 8.3) are 4.5 and 1.7 ml., respectively. The net titration of a standard aluminum solution containing the same quantity of ammonia or carbonate was high by the same 4.5 or 1.7 ml., respectively.

In Table II are summarized data calculated from titrations showing the effect of the presence of various substances.

Ammonia interferes strongly, but can be readily eliminated by volatilization upon boiling the alkaline solution.

Small quantities of carbonate interfere by being converted to bicarbonate at the final end point. Larger amounts will be converted to carbon dioxide when acidified, and lost, thus consuming proportionately more acid. Carbonate may be removed from the alkaline sample solution by treatment with excess barium chloride and rapid filtration with suction. The presence of the excess of the reagent does not influence the titration. The carbonate may be readily determined, if desired, by titration of the precipitate.

Moderate quantities of fluorides, which greatly interfere in the precipitation of aluminum hydroxide with ammonia, are without
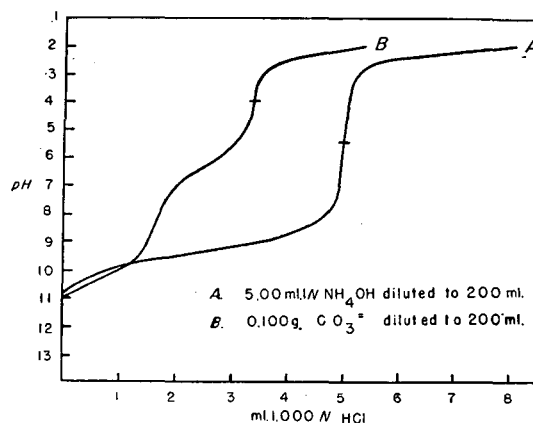
Figure 3.   Titration Curves

Table II. Effect of Ions on Acidimetric Determination of Aluminum

(0.2000 gram of Al plus addition in volume of 200 ml.)

Addition	Quantity	Net Titration	Al Found
	Mg.	Ml.	Mg.
None	...	29.70	0.2004
NH₃	4.65 ml. 1 N	34.00	0.2294
Na₂CO₃	5 CO₃⁻⁻	30.05	0.2027
Na₂CO₃	10 CO₃⁻⁻	30.00	0.2024
Na₂CO₃	25 CO₃⁻⁻	30.23	0.2039
Na₂CO₃	100 CO₃⁻⁻	31.35	0.2115
NaF	25 F⁻	29.80	0.2010
NaF	100 F⁻	29.79	0.2010
Na₃PO₄	5 PO₄⁻⁻⁻	29.86	0.2014
Na₃PO₄	100 PO₄⁻⁻⁻	29.93	0.2019
NaC₂H₃O₂	100 C₂H₃O₂⁻	29.90	0.2017
FeCl₃	10 Fe⁺⁺⁺	30.14	0.2033
Na₂SiO₃	4.5 SiO₂	30.05	0.2027
Na₂SiO₃	22.7 SiO₂	31.20	0.2105
Na₂SiO₃	91.0 SiO₂	29.40	0.1983

effect in the volumetric determination. Phosphate and acetate in moderate quantities have minor effects.

Both iron and silicate interfere by virtue of reactions with the fluoride added in the last step of the procedure. Iron forms the stable fluoride complex and the back-titration does not reconvert it to its original form, ferric hydroxide. Silicate forms fluosilicate and is converted to silica during the back-titration.

The method finds its greatest application in the determination of aluminum in sodium hydroxide solutions and provides a rapid means for determining aluminum in materials free from the interferences referred to above. It cannot be applied directly in the analysis of metals but may, in some cases, be employed to advantage after suitable separations.

PROCEDURE

Reagents. Standardized hydrochloric acid solution, 1.000 N. Standardized sodium hydroxide solution, 1.000 N. Barium chloride solution, 10 grams of barium chloride dihydrate per 100 ml. of water.

Potassium fluoride solution, 50 grams of potassium fluoride dihydrate in 100 ml. of water, neutralized to phenolphthalein. Retain in a paraffin-lined container.

Apparatus. pH meter with calomel and (high pH) glass electrodes. Mechanical stirrer.

Procedure. Take a sample of alkaline solution containing about 0.2 gram of aluminum. Transfer to a 250-ml. beaker containing sufficient barium chloride to precipitate carbonate completely from the liquor and sufficient water to give a final volume of about 175 ml.

Filter through a small Büchner funnel and wash the precipitate repeatedly with small portions of water until a total of about 100 ml. has been employed. In the analysis of sodium aluminate solutions containing little carbonate, it is unnecessary to filter unless more than a faint cloudiness of barium carbonate has formed. In this case, dilute the solution with 50 ml. of water and titrate directly.

Transfer the filtrate to a 600-ml. beaker and place it on the titrating assembly with stirrer and electrodes dipping in the solution. Start the stirrer and titrate with standard hydrochloric acid to the free sodium hydroxide end point. This is at a pH of about 11 and is determined accurately by interpolation as the point at which there is the greatest change of pH per 0.2-ml. increments of added acid.

Record the volume and calculate free sodium hydroxide if desired:

$$\text{Grams per liter of NaOH} = \frac{\text{ml. of HCl} \times 0.0400 \times 1000}{\text{ml. of sample}}$$

Continue the titration by the rapid addition of standard hydrochloric acid until the precipitated hydroxide has just redissolved and a very slight excess of acid is present. Add several drops of potassium fluoride solution to dissolve the last trace of precipitate; then add about 30 ml. more to precipitate cryolite. Add 4 to 5 drops of phenolphthalein and titrate with standard sodium hydroxide to the appearance of a pink color that holds for 15 seconds.

From the total hydrochloric acid addition, subtract the volume of the back-titration and the volume of the hydrochloric acid addition to the free sodium hydroxide end point. Record this volume as A.

$$\text{Grams per liter of Al} = \frac{A \text{ ml.} \times 0.027 \times 1000}{4 \times \text{ml. of sample}}$$

Notes. The free caustic end point is the point at which a permanent precipitate just starts to form. The quantity of excess acid, as measured by the back-titration, should not be over 1 to 2 ml. The distilled water employed must be essentially free from carbon dioxide.

If a carbonate determination is desired, the barium carbonate precipitate may be titrated in the conventional manner.

If a quantity of about 0.02 gram of aluminum is to be determined, the titration should be done with 0.1 N acid and base and the potassium fluoride addition reduced to 10 ml.

Aluminum in acid solutions may be determined by first adding saturated sodium hydroxide solution drop by drop until not more than 2 drops are present in excess of that required just to dissolve the precipitate. A saturated sodium hydroxide solution must be used because it is free from sodium carbonate by virtue of the slight solubility of the latter.

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Latex Strainability Test

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THE presence of fine coagulum in latex affects some processes very adversely. This coagulum is often wrongly blamed on some complicated chemical or physical action in the compound, when the true explanation is that all the larger particles were present in the original latex or dispersions from which the compound was made. The latex strainability test measures the amount of latex that will pass through a filter medium before clogging.

EQUIPMENT

The apparatus for making the test is constructed in the following manner:

A circle large enough to fit into the seat of a 0.5-inch aluminum pipe union is cut from 30-mesh stainless steel screen. The border of the screen is coated with rubber by dipping it in latex; this acts as a gasket. The exposed portion of the screen should be of

the same diameter as the inside of the pipe union. On this backing screen is placed a piece of standard felt cut to the dimensions of the screen. (The felt used in most of this work was No. 8805 from the American Felt Co., but any similar material could be used.) The parts of the union are then screwed tightly together and the union is fitted to a suction flask by means of a rubber stopper. The flask is connected by rubber tubing to a vacuum system containing a manometer and means for maintaining a vacuum of 125 mm. of mercury. At the start of the test, the suction flask is cut off from the vacuum by a pinchclamp.

DESCRIPTION OF TEST

To make the test on a material the felt should first be wetted thoroughly. First the pinchclamp is opened momentarily while 5 cc. of a 2% soap solution (usually potassium oleate) are poured through the felt. Then a measured volume (or weight if air bubbles are present) of the material under test is started through the felt. When the union is filled, the vacuum is applied by removing the pinchclamp. The material must be poured in fast enough to

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A method is described for measuring the amount of larger particles in natural and synthetic rubber latices, in dispersions to be used in compounding such latices, and in the compounds so made. Examples are given wherein the test is used to investigate the effect of variations in methods of handling raw latex and the effect of ball milling procedures on the quality of dispersions of compounding ingredients. A method is also outlined for using the test to detect interactions between the various dispersions used in compounding a rubber latex.

keep the felt always covered. This is continued until the felt chokes off. With unstrained latex or dispersion this end point is rather abrupt. With material that has previously been strained through felt, there is a gradual slowing down. In that case, the end point is considered to be reached when the time between individual drops of filtrate exceeds 5 seconds.

The strainability of the material under test is determined by subtracting the volume or weight remaining unfiltered after stoppage from the original volume or weight. This value is customarily converted to gallons per square foot of filter area, or some similar convenient dimensions.

FACTORS AFFECTING TEST

Various types of felts were examined to determine which was most suitable. These felts varied from very light to very dense materials with different amounts of wool. Since there was little variation in the results obtained by using the different types, the cheapest, No. 8805, was taken as standard.

The results in Table I were obtained on Sumatran centrifuged natural latex.

To determine the variability of the felt, twenty disks were cut at random from a 10-yard piece of felt, approximately 2 circles per yard. The strainability of another sample of the above type of latex was determined with each piece of felt and averaged 5.8 gallons per square foot with a standard deviation of 0.26 and a minimum and maximum of 5.3 and 6.3. To get such reproducibility, a 10-yard sample of felt should be set aside for testing only.

The strainability of a material is not independent of the applied pressure. Table II shows the effect of pressure drop on the strainability of another sample of the same type of latex. As the pressure drop increases, it tends to compress the felt, thus making it dense and decreasing the amount passed. A pressure drop of 125 mm. of mercury was taken as standard, since deviations of 25 or 50 mm. on either side affected the amount passed only slightly.

EXAMPLES OF USE OF TEST

On Raw Latex. To improve the behavior of latex in an extrusion process straining through felt was tried. The improvement could be followed by measuring the strainability of the .

Table I. Variations with Type of Felt

Felt	Wool %	Strainability Gal./sq. ft.
American Felt Co. 8805	25	7.6
American Felt Co. 8807	25	7.7
American Felt Co. 8820	25	9.7
American Felt Co. X293	...	8.3
American Felt Co. 70,105	100	7.8

Table II. Effect of Pressure Drop on Strainability

Pressure Drop across Felt Mm. Hg	Volume Passed Cc.
50	83
125	81
250	77
450	70
500	64
625	62

latex. The latex used was also Sumatran once-centrifuged material.

Once coagulum, sludge, etc., have been removed from well preserved latex, there is no spontaneous recurrence under ideal storage conditions. The strainability of some latex when freshly strained was 46 gallons per square foot. After storage for 2 months in a closed metal container, the strainability was 44 gallons per square foot. Any rapid decrease in the strainability of a latex is probably due either to outside contamination or to a reaction with added ingredients.

Table III. Strainability of Raw Latex

No. of Strainings	Strainability Gal./sq. ft.	Ratio: Present/Previous
0	8	...
1	41	5.13
2	69	1.68
3	80	1.16
4	105	1.31

In Making Dispersions. In attempting to improve the ball milling of dispersions to be used in latex compounding by either changes in procedure or formulation, it is difficult to know when an improvement has been made. The strainability test offers a useful tool. For example, in studying the effect of ball milling time and ball mill loading on a sulfur dispersion the following tests were made: A 150-gallon ball mill was used for each test, loaded in each series with 625 pounds of flint pebbles. In the first case, the mill charge was 1200 pounds of wet dispersion and in the second, 395 pounds. Table IV gives the resulting strainabilities.

Table IV. Strainability of Sulfur Dispersion

Time of Milling, Days	Strainability, Gallons per Square Foot	
	1200-lb. loading	395-lb. loading
1	...	1.0
2	0.3	5.0
3	0.3	5.8
4	0.3	5.9
5	3.6	...
6	5.1	8.2
7	4.2	8.9
8	5.8	10.2
9	5.4	...
10	5.0	...
11	6.4	...
12	...	...
13	6.5	...
14	7.6	...
15	6.8	...

These data indicate that lowering the weight of a ball mill charge is very effective for increasing the efficiency of sulfur grinding.

Strainability measurements may be used as a control test on factory batches of dispersions for latex compounding.

In Latex Compounding. If we consider the straining of a mixture of ingredients, A and B, which do not interact, the two ingredients can be thought of as straining through separate areas of felt. Then the total area of felt required to strain the mixture will be the sum of the two separate areas.

Table V. Compound Strainability

No.	Ingredient	Strainability Gal./sq. ft.	Amount Added Gal.
A	Neoprene latex (Type 571)	77.0	12.00
B	Stabilizer solution	∞	0.80
C	Zinc oxide dispersion	16.8	1.00
D	Filler dispersion	17.5	2.00
E	Antioxidant dispersion	2.8	0.25
F	Pigment dispersion	8.3	1.00
	Total compound	35.0 (experimental)	17.05

For example, mix a gallons of A with a strainability of S_1 requiring a/S_1 square feet of felt with b gallons of B with a strainability of S_2 requiring b/S_2 square feet of felt. Then $a + b$ gallons of mixture with a strainability of S_T requiring $(a+b)/S_T$ square feet of felt will result.

Thus $\dfrac{a}{S_1} + \dfrac{b}{S_2} = \dfrac{a + b}{S_T}$, or for any number of noninteracting

ingredients A, B, C, D, . . . of a, b, c, d, . . . gallons each $\dfrac{a}{S_1} +$

$\dfrac{b}{S_2} + \dfrac{c}{S_3} + \dfrac{d}{S_4} + \ldots = \dfrac{a + b + c + d + \ldots}{S_T}$ where S_T is the strainability of the mixture.

By comparing the last equation with strainability results obtained during latex compounding, interactions between ingredients can be detected.

The data in Table V indicate a compound produced without interaction.

By the noninteraction formula

$$\frac{12.00}{77.0} + \frac{0.80}{\infty} + \frac{1.00}{16.8} + \frac{2.00}{17.5} + \frac{0.25}{2.8} + \frac{1.00}{8.3} = 0.5393 = \frac{17.05}{S_T}$$

$$S_T = \frac{17.05}{0.5393} = 31.6 \text{ gallons per square foot, which agrees}$$

fairly closely with the experimental result and indicates little or no interaction.

ACKNOWLEDGMENT

The authors wish to acknowledge substantial contributions to the early work on this subject by A. R. Brosi, R. H. Walsh, and R. G. Seaman, all formerly of this laboratory.

Identification of Crystalline Progesterone with 2,4-Dinitrophenylhydrazine

Quantitative Determination of Progesterone in Oil

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A procedure is described for identification of crystalline progesterone by quantitative precipitation of a derivative with 2,4-dinitrophenylhydrazine. Evidence is presented that the reaction product of progesterone with 2 molecules of 2,4-dinitrophenylhydrazine is a monopyrazoline-monohydrazone. The method developed is suitable for the gravimetric determination of pure progesterone in oil. Results of analyses show excellent recoveries of crystalline progesterone by itself and when added to oil. Analyses of commercial samples of pure progesterone in oil yielded values close to the labeled amounts.

IN THE course of preparing crystalline progesterone in a vegetable oil for parenteral use, it was necessary to determine the progesterone content of the oil preparations for analytical control purposes. A recent review (3) shows the inadequacies of present chemical methods. Any specific chemical methods which could be developed would have obvious advantages over bioassay procedures (1). With the ketonic reagents available, a chemical assay method seemed possible. The Hughes procedure (6) with Girard reagent T was first tried but quantitative recoveries from oil could not be obtained. The determination of estrone with 2,4-dinitrophenylhydrazine (8) then suggested this reagent for the estimation of crystalline progesterone. No information regarding previous use of this hydrazine for the identification and determination of the hormone of the corpus luteum could be found.

Progesterone with two carbonyl groups reacts as expected with two molecules of 2,4-dinitrophenylhydrazine. Evidence is adduced that the compound formed is a monopyrazoline-monohydrazone, isomeric with the expected progesterone, bis(2,4-dinitrophenylhydrazone). This derivative may be either 3,5-{3'-[2'-(2''',4''-dinitrophenyl)]pyrazolyl}pregnene-3-one-20,2''',4'''-dinitrophenylhydrazone (Ia), or 3,5-{2'-[1'-(2'',4''-dinitrophenyl)]pyrazolyl}pregnane-one-20,2''',4'''-dinitrophenylhydrazone (Ib).

In attempting to demonstrate the chemical relationship of the derivative to progesterone by acid hydrolysis and recovery of the parent compound, no progesterone was isolated under a variety of conditions employed. In fact, the extreme insolubility of the derivative necessitated prolonged periods of heating to dissolve the compound, apparently by reaction. The reaction product was a lower melting compound (decomposition point, 150° C.) corresponding to a mono-2,4-dinitrophenylhydrazone. Treatment of this mono-compound with 2,4-dinitrophenylhydrazine regenerated the original derivative described above (decomposition point, 282–283° C.), thus demonstrating that the second, difficultly hydrolyzable, hydrazine residue has the same structure in both compounds. The great resistance to hydrolytic cleavage of the second hydrazine residue suggests a cyclic structure involving the conjugated system of the 3-keto-Δ-4,5 structure of progesterone. This cyclization reaction appears to be general in simple conjugated systems (4, 7), and its occurrence can be deduced from the facts presented. No evidence is available for a choice between the two alternate structures, Ia and Ib. The hydrolytic cleavage product may also have alternate structures.

Regardless of the structure of the derivative, the conversion factor for the weighed precipitate to progesterone is the same: 0.466.

The derivative is insoluble in water, ethanol, and hexane. Vegetable oils are immiscible with 90% ethanol, whereas progesterone is soluble in this concentration of alcohol. These properties permit gravimetric determination of progesterone in oil solution.

Ia   Ib
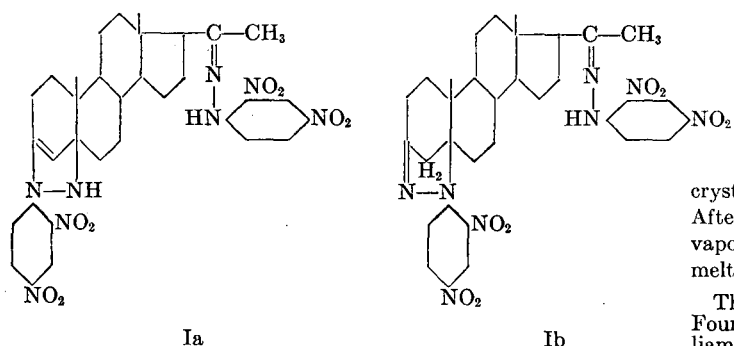
PROGESTERONE METHOD

The following analytical procedure was adopted for the determination of progesterone in oil.

Apparatus. Separatory funnels of 125-ml. capacity, glass-stoppered. Erlenmeyer flasks of 125-ml. capacity, standard taper, with pourout lip. Reflux condensers, standard taper. Filter crucibles of 20- or 30-ml. capacity, 10 porosity Selas or equivalent.

Reagents. Mixed hexanes, approximate boiling point range 55° to 70° C. Ethyl alcohol, specially denatured absolute or 95%, containing 0.5% benzene. Ethyl alcohol, 90%. 2,4-Dinitrophenylhydrazine. Hydrochloric acid, concentrated. Hydrochloric acid, approximately 0.5 N.

Extraction of Progesterone from Oil Solution. Measure a portion of the oil solution, containing about 20 mg. of progesterone, into a separatory funnel. Depending on the volume of the oil taken, usually between 2 and 20 ml., add 20 to 40 ml. of hexane. Extract the hexane solution five times with 10- to 20-ml. portions of 90% alcohol, combine the alcohol extracts in an Erlenmeyer flask, and evaporate to dryness on a steam bath with the aid of a current of air.

When progesterone is determined in pharmaceutical preparations, no difficulty from interfering substances is met in those containing only progesterone. In pharmaceutical preparations containing estrone and progesterone, advantage may be taken of the extractability of the estrone from hexane solution by 2 N sodium hydroxide as in the method of Carol and Rotondaro (2). Progesterone may then be determined on the estrone-free hexane solution.

Preparation of 2,4-Dinitrophenylhydrazine Derivative of Progesterone. To the residue or to a weighed sample of pure progesterone, add approximately three times its weight of 2,4-dinitrophenylhydrazine, followed by 30 ml. of ethanol, absolute or 95%. Connect the condenser to the flask and reflux on a steam bath for 15 minutes. Add 1 ml. of concentrated hydrochloric acid, and continue refluxing for 15 minutes more. The hydrazone precipitates either upon the addition of the acid or during the second refluxing period. Cool the mixture to room temperature and filter off the precipitate in a previously tared filter crucible. Wash the precipitate carefully with two 10-ml. portions of ethanol, followed by six 10-ml. portions of hexane. Since this solvent removes any oil trapped in the precipitate, it is omitted when the extraction from oil solution is not used. To remove any unreacted hydrazine wash with 5-ml. portions of alcohol, then with 0.5 N hydrochloric acid, until the filtrate comes through colorless. Remove the residual acid by washing with distilled water. Finally transfer the filter and contents to a desiccator and dry in vacuo to constant weight over a drying agent—e.g., Drierite. Weigh on an ordinary analytical balance.

The precipitate formed is deep orange-red in color. The weight of the precipitate × 0.466 = mg. of progesterone in the sample taken.

RECOVERIES AND IDENTIFICATION OF PROGESTERONE DERIVATIVE OF 2,4-DINITROPHENYLHYDRAZINE

A series of samples of crystalline progesterone (melting point 128.5–129.5° C.) was precipitated by the method outlined. The results are summarized in Table I. Recoveries obtained (99.9 ± 0.7%) show that progesterone reacts with 2 molecules of dinitrophenylhydrazine to yield a weight of precipitate that agrees with the theoretical values.

This derivative gave melting point values with decomposition, ranging from 271° to 278° C. (Table I). [Melting points, corrected, were taken with the Hershberg apparatus (5) using completely immersed, uncalibrated, Anschütz thermometers.] The combined precipitates were twice recrystallized by solution in toluene and dilution with ethyl alcohol. Both first and second recrystallized products decomposed without melting at 282–283° C. After the purified product was dried in vacuo over xylene vapors in an Abderhalden drying tube, it still had the same melting point.

Theory ($C_{33}H_{38}N_8O_8$): C, 58.75%; H, 5.68%; N, 16.60%. Found: C, 58.3%; H, 5.4%; N, 16.55%. Analysis by William Saschek, Columbia University, College of Physicians and Surgeons, New York, N. Y.

STRUCTURE OF 2,4-DINITROPHENYLHYDRAZINE DERIVATIVE OF PROGESTERONE

Preliminary experiments were carried out to determine the least drastic conditions for carrying out the acid hydrolysis. Mixtures of hydrochloric acid with the following organic solvents were employed: glacial acetic acid, n-butyl alcohol, isobutyl alcohol, and ethyl alcohol. In all cases deep orange residues were isolated, insoluble in 2 N hydrochloric acid and soluble in ethyl ether and ethyl alcohol. The lowest refluxing temperature could be obtained with acid–ethyl alcohol mixture.

Approximately 150 mg. of the dihydrazine derivative of progesterone were refluxed for 66 hours with 600 cc. of ethyl alcohol–6 N hydrochloric acid mixture (3 to 1). The long heating period was required to dissolve the compound. After evaporation to dryness in vacuo the residue was taken up with 350 cc. of ethyl ether. The ether solution was extracted with 2 N hydrochloric acid, washed with distilled water, and dried with anhydrous sodium sulfate. After removal of the solvent, the residue was recrystallized three times by solution in ethyl alcohol and dilution with water. The product had a deep orange-red color.

The products obtained after the second and third recrystallizations exhibited similar melting point properties. Decomposition with softening started at about 150° C. and decomposition was not complete until about 170° C. After drying in vacuo over

Table I. Analysis of Progesterone with 2,4-Dinitrophenylhydrazine

Progesterone Taken	Dinitrophenylhydrazine Derivative Recovered		Progesterone Recovered	
Mg.	Mg.	M.P., ° C.	Mg.	%
25.7	54.7	275–6	25.5	99.2
44.0	94.5	271–2	44.0	100.0
37.7	80.1	275–6	37.3	99.8
61.1	131.4	277–8	61.2*	100.1
35.6	76.6	276–7	35.7	100.2
30.6	65.6	275–7	30.6	100.0

Table II. Analysis of Progesterone in Oil[a]

Identification of Sample		Dinitrophenylhydrazine Derivative Recovered		Progesterone Recovered	
Progesterone taken	Sesame oil taken				
Mg.	Cc.	Mg.	M.P., ° C.	Mg.	%
18.9	2	40.3	276–7	18.8	99.4
20.1	5	45.0	273–4	21.0	104.4
28.3	5	60.9	273–4	28.4	100.3
18.9	10	40.7	273–4	19.0	100.5
30.1	15	63.8	274–5	29.7	98.8
18.9	20	40.3	270–1	18.8	99.4
20.1	20	43.2	270–1	20.1	100.0

Progesterone in Oil (Commercial)

Labeled Amount of Progesterone					% of labeled amount
Mg./cc.					
5	5	56.1	273–4	26.1	104.5
5	5	54.6	271–3	25.4	101.8
5	5	55.8	272–3	26.0	104.0
5	5	54.8	276–8	25.5	102.0
5	5	54.8	274–6	25.5	102.0
10	2	43.5	272–3	20.2	101.0
10	2	44.0	271–2	20.4	102.0
10	2	42.1	278–9	19.6	98.0
10	2	41.8	276–7	19.5	97.5

[a] Some determinations done by A. Albamonte.

water in an Abderhalden dryer, a nitrogen determination was carried out. As postulated this compound contained one dinitrophenylhydrazine residue with an empirical formula of $C_{27}H_{34}N_4O_5$. Nitrogen found 11.97%, theory 11.32%.

Approximately 10 mg. of the hydrolytic cleavage product and an equal quantity of 2,4-dinitrophenylhydrazine in 5 cc. of ethyl alcohol were made to react as in the progesterone determination. The resulting orange-red precipitate, without being recrystallized, melted with decomposition at 276.5° C. Mixed with the pure dihydrazine derivative of progesterone, melting point with decomposition was 279–281° C.

DETERMINATION OF PROGESTERONE IN OIL

Progesterone was added to sesame oil, and recovery determinations were carried out. Results shown in Table II are similiar to the recoveries and melting point values of the derivative obtained with pure crystalline progesterone (Table I). Application of the method to oil solutions for control purposes yielded values in agreement with the labeled amounts (Table II).

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Boron Microdetermination in Fresh Plant Tissue

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Boron is extracted from 5 sq. cm. of leaf at room temperature, with a mild chemical extractant, in the same dish in which the color is to be developed. This prevents possibility of contamination from boron in filter papers and loss of boron at elevated temperatures. A sampling device is described for cutting four foliage strips 2.5 × 25.0 mm. at one time; eight such strips constitute the sample for extraction. Representative sampling is effected by using a single strip from each one of eight leaves. Where advisable, foliage can be gathered, prepared, and extracted, and the color developed and read within one working day. The normal range is from 0.2 to 1.2 microgram of boron per determination.

IN THE analysis of soils and plants for boron, where submicrogram levels are routinely encountered, great care must be exercised against contamination. In sample preparation, especially of plants, equal attention must be given to retention in the sample of the small but very essential amount of boron initially present. A discussion of the major causes of contamination and loss is presented, preliminary to an analytical procedure designed to eliminate these difficulties.

In an early attempt to study plant uptake of boron as related to soil applications, valid differences were obscured in analysis by a heavy and variable background contamination. High quality double-acid-washed filter paper was found responsible for this contamination and its use in boron microanalysis was discontinued in January 1943. Twelve widely used filter papers have been analyzed for boron content (Table I). A composite sample of each kind consisted of four 90° segments obtained one each from 4 disks selected at random through the pack. These were torn roughly into centimeter squares and extracted as indicated in Table I, with occasional stirring. Duplicate determinations were made, using 1-ml. aliquots from these solutions.

The data in Table II were obtained by placing a Whatman No. 40 paper in a Kimble 58° funnel, using the conventional method of folding. The successive 10-ml. portions of solution were delivered from a pipet, the tip being directed in a circle just below the rim of the paper. Each portion was caught in a separate size 00 Coors porcelain dish, and boron was determined in the usual manner. The high amount of boron in filter paper, as shown in Table I, and the ease with which it is carried into the filtrate (Table II) constitute sufficient reason for avoiding its use. On the other hand, the residual value of 1.95 micrograms after seven washings (Table II) suggests that prior washing of the paper before filtering an unknown may not give adequate protection against contamination from that source.

The apparatus shown in Figure 1 was used to study the amount of boron volatilized from pecan foliage during normal, carefully regulated drying and ashing.

A size 00 Coors porcelain evaporating dish was employed for the lower half of the retort, R, while a 65-mm. Kimble 58° funnel with stem bent as shown was used for the upper half. Concentric-style ring clamps attached to a short piece of iron rod were used to hold these together as a rigid unit. Volatilized materials were conducted away through a 9-mm. soft-glass tube, T, into soft-glass 32 × 160 mm. centrifuge tubes, used as condensing tubes, each containing 12 ml. of a 0.1 N suspension of calcium hydroxide.

One gram of fresh leaf tissue was placed in the lower half of the retort, and, after the two condensing tubes, A and B, were connected slow aspiration was applied. A third tube was used in the series experimentally, but was found unnecessary, as most of the boron was stopped in A, the remainder in B. In this manner foliage from the borax-treated tree (Figure 2) was raised through successive temperatures in such a way as to allow the

Table I. Easily Extractable Boron in Standard Filter Papers[a]

No.	Make	Maker's No.	Quality (Acid Wash)	Size, Cm.	Ash Weight, Gram	Micrograms of Boron per Paper
1	Whatman	4	None	9	0.00052	1.80
2	Whatman	1	None	9	0.00039	5.80
3	Whatman	2	None	11	0.00880	65.60
4	Whatman	31	Single	11	0.00033	7.00
5	Whatman	30	Single	9	0.00021	4.80
6	Whatman	32	Single	11	0.00031	8.20
7	Whatman	41	Double	11	0.00015	7.20
8	Whatman	40	Double	11	0.00013	7.80
9	Whatman	42	Double	9	0.00006	3.60
10	Schleicher and Schüll	595	None	11	Not stated	8.80
11	Schleicher and Schüll	597	None	11	0.00340	14.40
12	Schleicher and Schüll	5893	Double	9	0.00005	17.60

[a] Extracted 2.5 hours at room temperature in 250-ml. boron-free beakers, using 20 ml. of a solution 0.125 N in respect to HCl and 0.0125 M in respect to KCl.

Table II. Easily Extractable Boron Remaining in Filter Paper[a] after Successive Washings

Wash No.	Wash Solution	Volume Used Ml.	Boron Removed Micrograms	Extractable Residual
1	As in Table I	10	4.00	....
2	As in Table I	10	1.35	....
3	As in Table I	10	0.68	....
4	As in Table I	10	0.58	....
5	Water	10	0.34	....
6	Water	10	0.25	....
7	Water	10	0.34	....
By same procedure as in Table I				1.95

[a] Whatman No. 40, 11 cm.

material first to become completely dry, then gradually to approach the ashing range. The two lowest temperatures were obtained in a thermoregulated electric oven, then the retort was transferred into an electric muffle furnace as shown. The length of each period, beginning with 100°, was 2, 2, 2, 2, and 4 hours. In general, the first hour in each period was used to bring to the temperature indicated, the following time in maintaining at that temperature. At the conclusion of each period the condensing assembly (tubes T, A, and B) was removed and another having tubes A and B freshly charged with calcium hydroxide suspension was substituted. Blanks were run in the same manner, except that no plant material was present in the retort. Positive but low values were obtained and were subtracted from the corresponding foliage values.

The summation of values from tubes A and B for each period is presented in Figure 2, together with the boron determined in the same way by ashing pecan foliage from a check tree (not treated with boron) for 6 hours at 450° C., following a drying period of 5 hours at 80° C. These data establish clearly that boron is lost not only during ashing but also in some cases at temperatures as low as 100° C. While only about 4% of the total boron was lost in these instances, this was under ideal conditions with a dense foliage containing initially only 53% moisture.
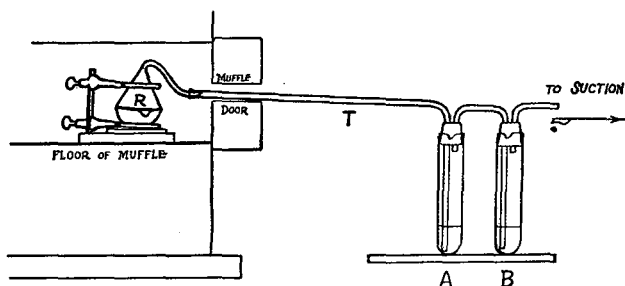
Figure 1. Apparatus for Collecting Boron Volatilized from Plant Tissue at Elevated Temperatures

Unless special preventive measures are taken in the drying of succulent foliage samples, there is a tendency for groups of leaves as they become thoroughly wilted to coalesce, forming a somewhat solid mass. There is then prolonged retention of moisture accompanied by internal heating, often followed by sloughing of tissue and the loss of highly volatile products not originally present. Many boron compounds are rather easily volatilized—for example, boric acid is volatilized by steam, while its two lowest trialkyl esters boil at 65° and 120° C.; the compound $B(CH_3)_3$.-NH_3 boils at 110° C., and trimethylboron is a gas at ordinary temperatures. Therefore, it is conceivable that even where the above described conditions occur in moderate degree they may cause some loss of boron during the drying period, and predispose to more than normal losses at the elevated temperatures required for ashing.

While the errors discussed have been those of loss or contamination, related in some way to sample preparation, there was found in the turmeric micromethod a persistent fault resulting

from variable amounts of very finely divided lime in the final colorimetric solutions. The resulting cloudiness is masked by the yellow color of the solutions and may not be apparent to the eye, but in a photoelectric colorimeter it can cause high and variable errors. Careful study revealed that the excess reagent lime in the determination could be made to precipitate in a dense flaky mass by the addition of a small and constant amount of a potassium salt. This precipitation occurs in the routine operations, without introducing complexity, and the color reaction appears to be sensitized by the favorable physical conditions induced by this salt in the second (color-forming) evaporation. In the extraction method as originally employed, and as outlined herein, the above error is eliminated by using the required amount of potassium chloride as one of the ingredients in the extracting solution.
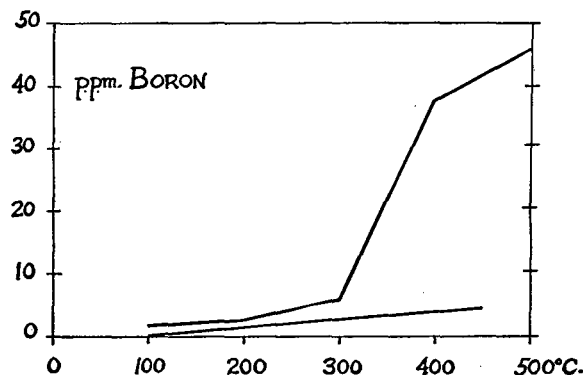
Figure 2. Boron Volatilized from Pecan Foliage at Various Temperatures

Upper. Losses from foliage of borax-treated tree
Lower. Losses from untreated tree

Since titanium, molybdenum, and zirconium as their respective acids produce a brown color with turmeric test paper, there might be reason to question the specificity of the turmeric method for boron. As a means of checking for possibility of interference, salts of the above metals were used to give 1, 10, 100, and 1000 micrograms of the element per determination, for testing by the routine procedure as used for boron. Colors developed in all instances, particularly with titanium. These colors were rather intense while in the dishes, but when taken up with 95% ethanol they paled to approximately the same intensity as the blank, showing no interference. Sulfite also was tested over the above range, to determine what effect it might have if present as a residual processing agent in filter papers. Its effect upon color was negative, all determinations showing less intensity than the blank. From the above study it appears that the turmeric method is satisfactorily specific for boron.

In the procedure outlined below, boron is extracted directly from the fresh plant tissue, at room temperature, in the same dish in which the color is later developed. This has eliminated the usual dangers from contamination and loss. The sample consists of eight strips, 2.5 mm. wide and 25.0 mm. long. All strips may be from one leaf, where the sample material is limited, or they may represent a sample consisting of eight individual leaves. A multiple-blade knife is used for cutting these strips quickly and accurately to size (see Figure 4). While only about 40% of the boron is extracted by this procedure, it is extracted dependably, giving high reproducibility and excellent correlation with soil applications of borax. The final colorimetric determination is done by a modification of the method of Naftel (2).

EQUIPMENT

Glassware. All glassware, including reagent bottles, should be of boron-free glass. Corning No. 728 has proved very satisfactory. Possible exceptions may be in the use of Exax pipets

and 15-ml. graduated (pointed) centrifuge tubes of ordinary soft glass. The stirring rods used during the extraction period should be of soft glass, about 4.5 × 80 mm. Pyrex should be avoided at all stages, because of its high boron content. All glassware and porcelain should be thoroughly acid-leached before using.

Evaporating Dishes. Coors size 00, new. From twice the number required, those showing the least deviation from the mean weight should be selected to ensure uniform evaporation and greater accuracy.

Balance Weight Forceps. Fisher, stainless steel.

Water Bath. An electrically heated and regulated water bath has been found indispensable for precise results. It should have not less than 21 openings, each approximately 65 mm. in diameter. One opening may be used for inserting the propeller of a circulating device unless the bath is so equipped. The bath should be filled half-way with water for the first evaporation (100° C.), then when filled all the way for the color-developing evaporation, will have its temperature reduced to about the required 56° C.

Photoelectric Colorimeter. The Fisher Electrophotometer employing the micro assembly and micro absorption cells has been found very satisfactory. The 525-B filter should be used, the light intensity set at B, and the "initial null" knob turned all the way to the left and blocked. To avoid optical differences the same two cells should be used always in the same positions, facing in the same direction, and blocked so they cannot rotate. They may be filled and emptied by a 10-ml. pipet having a rubber bulb at its upper end. Because of the colored blanks a complete "null" of the instrument is impossible unless factory settings are disturbed. Therefore, a reading for the blank should be set down against each unknown reading and subtracted from it. When all reagents are relatively boron-free a blank value of below 10 is normally obtained.

REAGENTS

Extracting Solution. A stock solution is prepared by thoroughly mixing equal volumes of 1.0 N hydrochloric acid and 0.1 molar potassium chloride. The extracting solution is prepared as required by mixing 1 volume of the stock solution with 3 volumes of water.

Calcium Hydroxide. A saturated solution is prepared by shaking 2 grams reagent-grade calcium hydroxide in 1 liter of water, allowing it to settle several days, then removing the clear supernatant by slow suction into another bottle for routine use. It seems impossible to obtain boron-free calcium hydroxide. The most practicable adaptation is to test several lots, and use the one giving the least contamination. The prepared solution should be shaken thoroughly each time just before using, then measured equally into all determinations. Boron contamination introduced into an unknown is canceled by an equal contamination in the blank.

Oxalic Acid Mixture. To 24 ml. of saturated oxalic acid in a 250-ml. Erlenmeyer flask are added 8 ml. of concentrated hydrochloric acid and 8 ml. of water, in that order. The flask should be swirled at once to mix the solution, then set into a 600-ml. beaker containing 200 ml. of water at about 45° C. The solution should be used soon after preparing.

Turmeric Solution. One gram of turmeric powder in 100 ml. of 95% ethanol is allowed to extract, in a 500-ml. Erlenmeyer flask, with occasional shaking for 1 hour or longer. One hour before the solution is needed this flask should be placed in a nearly horizontal position, resting in the rim of a 600-ml. beaker. After 30 minutes, if lifted and poured without disturbing, a reasonably clear solution will result. A second decantation done in the same manner gives the final clarification.

Distilled Water. The product of several different types of Barnstead all-metal stills has been found satisfactory.

PROCEDURE

Place the eight foliage strips in a dry Coors size 00 porcelain dish, pipet 4 ml. of the extracting solution (at 25° C.) over them, and start timing the extraction. Stir with the glass rod until the strips are reasonably well wetted, thereafter at about 5-minute intervals. After 25 minutes collect the eight strips together near the side of the dish opposite the lip, gathering them into a parallel group, with ends about even. Rest the glass rod in the lip of the dish, so its lower end holds the strips in position.

After the extraction period is finished (30 minutes), use the glass rod to draw the group of strips up the side of the dish, clear of the solution, and in a vertical position with their upper ends somewhat above the rim. After draining about 5 minutes take them up with the stainless steel forceps and rinse by holding slightly above the extracting solution and pouring over them slowly, from a 15-ml. centrifuge tube, an amount of calcium hydroxide solution which, by previous determination, has been found necessary to neutralize 4 ml. of the extracting solution, using phenolphthalein as the indicator. (For convenience, when a
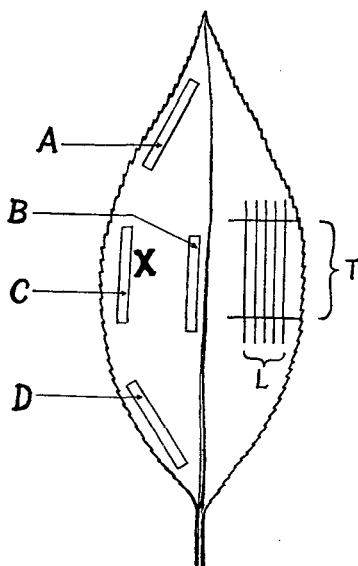

Figure 3. Zonal Deposition of Native Boron in Pecan Foliage

A, 2.71; *B*, 1.95; *C*, 3.14; *D*, 2.93 micrograms per 10 sq. cm. Right half, four sample strips cut at one time by *L* blades of sampling knife. Transverse cuts (for correct length of strips) made by *T* blades. Strips are to relative scale in a leaflet 50 × 125 mm.

number of extractions are being made at one time, the required amount of calcium hydroxide should be measured into the centrifuge tubes before the extraction is begun and the tubes stoppered with cork.) After rinsing, drain the foliage strips by touching their tips at several points to the inside walls of the dish, then discard them. Stir the solution with the stirring rod which was allowed to remain in the dish, then drain it similarly and remove. Place the dish on a steam bath at full temperature and evaporate until dry. Remove and cool to room temperature.

Add 1 ml. of the oxalic acid mixture, and rotate until the interior of the dish is thoroughly washed down. Add 2 ml. of the turmeric solution, rotate without delay, and place at once on water bath previously thermostatically regulated to 56° C. The dish should rest in the bath with its contents below the surface of the water. Protect completely from stray air currents and from direct sunlight, and do not disturb the dish during the evaporation, which should require about 1 hour. Allow to go to complete dryness—i.e., until no extensive maroon-colored areas remain in the bottom of the dish. Remove, chill in refrigerator, then add 6 ml. of 95% ethanol from a pipet, guiding the tip two or three times around inside rim of dish to wash down color from side walls. Allow to stand about 5 minutes, then swirl several times, allow to settle, and pour into a 15-ml. graduated centrifuge tube, allowing caked material to remain in dish. Rinse dish with 4 ml. of ethanol in similar manner, transfer to tube, then if necessary add more ethanol to make to 10 ml. Stopper tube with cork, shake thoroughly, and centrifuge at moderate speed for 10 minutes. The solution is now ready to be read. Compare against a calibration curve prepared from standards of boric acid, using 1 to 6 ml. of a solution in which 1 ml. is equivalent to 0.2 microgram of boron. Develop the color as indicated for the unknowns, including in every instance 4 ml. of the extracting solution, which is necessary to ballast and regulate the reaction. Report all determinations as micrograms of boron per 10 sq. cm. of foliage. Twenty determinations (including two blanks) can be run at one time.

Because of the high sensitivity of the reaction, the boron extracted from foliage grown at above-normal levels may give a color too intense to read. When this condition is known or suspected, the following adaptation should be observed:

At the conclusion of the extracting period rinse the foliage strips with 3 ml. of extracting solution, delivered from a pipet, instead of calcium hydroxide. Transfer the now 7 ml. of plant extract into a 10-ml. glass-stoppered volumetric flask, rinse dish into flask with three successive 1-ml. portions of extracting solution, adjust to 10 ml., and shake thoroughly. Pipet a suitable aliquot into a fresh dish, usually 1 to 4 ml. (never more than 4). If 4 ml., it contains the necessary equivalent of 4 ml. of extracting solution and is ready for addition of the necessary calcium hydroxide solution. If less than a 4-ml. aliquot is used, enough extracting solution must be added to bring it up to 4 ml. before the calcium hydroxide is added. The determination is then carried out in the usual way and the result multiplied by the proper restoring factor, a 1-ml. aliquot being multiplied by 10, a 2-ml. aliquot by 5, or a 4-ml. aliquot by 2.5.

SAMPLING

The following sampling practice has given very satisfactory results in pecan foliage analysis (17-year-old trees):

Eight leaves were taken at equidistant positions around each tree, 12 to 16 feet above the ground, avoiding terminal growth. As the pecan leaf is compound, consisting of a terminal and several opposite pairs of leaflets, one leaflet was selected for the sample, from the pair nearest the terminal. The eight selected leaflets were rubbed against a flat aluminum sieve of 2-mm. perforations under a flowing tap to remove spray residues, then rinsed with distilled water and allowed to drain 10 to 30 minutes before the sample strips were cut.

In preliminary tests with tung foliage, boron concentration was found to vary with position in the leaf, being greatest in the peripheral zones. A similar study was made with pecan foliage collected late in the summer from a tree which had received no boron supplement. From each of eight leaflets constituting the sample, a strip was cut at position A (see Figure 3). These eight strips were placed in a dish, ready for extraction, while similar strips were cut from positions B, C, and D. Duplicate determinations were prepared by cutting strips from corresponding positions in the other halves of these same leaflets. The mean values from each of these four positions are given in connection with Figure 3. From these data it was concluded that for routine sampling, in order to obtain a representative sample, the strips should be cut at position X (Figure 3). It is believed that this position, half-way from base to tip of leaf, and two thirds the distance from midrib to margin, will be satisfactory for all foliage of similar configuration.

The sampling knife (Figure 4) facilitates and ensures quantitative accuracy in preparation of samples for extraction.

The cutting edges are Star single-edge razor blades mounted in such a manner as to be easily replaced when dull. Transverse metal pins (finishing nails cut to suitable length) placed through the notches in ends of the five blades at the L end gage them to proper depth, while the two slender stove bolts clamp them in place. At the T end the two blades are attached to the wooden handle by 3 $\times$ 12 mm. round-head brass screws. Only screws R are removed in replacing blades at the T end of handle, screws F having grooves made beneath the heads (all the way around the shank), so notches in blades can fit into them. Screws R fit tightly against but only part-way into the notches in the opposite end of blades. The reinforcing strips along backs of blades should be recessed into handle at points of contact—i.e., outside of T end, and inside of L end. Spacing block S, approximately 9 $\times$ 40 mm. by 4 mm. deep, is set into the handle above backs of blades to keep side pieces from compressing too much at that point.

The individual spacers between blades (L end) are shown to scale. They may be made from wooden plant labels as used in greenhouses, and should be about 2.4 mm. thick. If a little
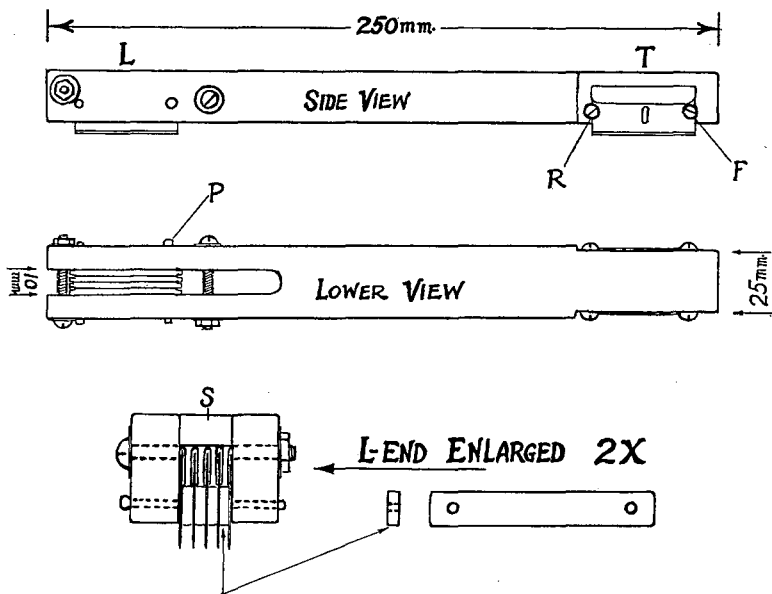
(Soil sampled 0 to 14 inches deep, values expressed as p.p.m. of boiling water–extractable boron in dry sample. Foliage boron as micrograms of extractable boron per 10 sq. cm. of leaf)

Tree No.	Borax, Lb. per Tree (June 7)	Soil B as of Aug. 21	Foliage B as of Sept. 10	Soil B as of Sept. 18	Foliage B as of Oct. 2
11	0	0.10	2.66	0.11	2.90
12	0.5	0.15	3.80	0.14	4.26
10	1	0.54	6.12	0.47	7.12
8	2	0.82	7.62	0.67	8.12
13	4	0.98	13.50	0.83	14.76
6	8	2.12	14.76	2.28	15.88
9	16	5.33	22.50	5.84	29.00
Inches of rainfall since borax applied (June 7)		27.02	31.26	33.76	34.05

too thin to give the exact 2.5-mm. spacing (centers) to L blades, they can be built up with coatings of Duco cement; if too thick, they can be dressed down slightly with a fine file. When finished they are held permanently in place by pin P, only the stove bolt and pin at extreme end of handle being removed when the L blades are replaced. The cutting edges of all blades should be exposed about 4 mm. below the lower face of the handle.

After foliage samples are washed and drained as described, strips are prepared as shown in right half of Figure 3. One leaf at a time is placed upon a cutting board of soft cypress or similar wood, the "points" of the blades (L end) are pressed firmly upon it, the opposite end of the handle is elevated about 20°, and the blades are drawn along the leaf for more than the required 25 mm. The handle is then reversed and the T blades are used to cut the resulting four strips to proper length. This cut is made by pressing the two blades downward upon the board until the strips can be lifted free (Figure 3). In routine analysis the two strips corresponding most nearly to position X are selected, and the other two discarded. The two strips saved are placed in separate dishes, and after the above technique is followed for the eight leaves in the sample, there are eight strips in one dish and eight nearly identical strips in the other—thus giving the "duplicates." If eight leaves are not considered sufficiently representative, sixteen can be used in each sample, and one strip saved from each. If only a single leaf is to be analyzed, four strips are cut from each half, as shown in right half of Figure 3.

When a number of samples are being analyzed, all should be washed and drained at one time. Then after the strips from each are cut and in dishes, they are covered with watch glasses, which conserve moisture while the other samples are being similarly prepared. Foliage to be transported long distances to a central laboratory for analysis should be placed in screw-cap glass jars just large enough to hold the eight leaves of a sample without folding. They can be held at ordinary temperatures for a considerable time without wilting, but preferably for not more than 20 hours.

EXPERIMENTAL

This procedure was first extensively applied through the summer of 1945 in determining the uptake of boron by 17-year-old Stuart pecans following soil applications of borax on June 7 at the rate of 0, 0.5, 1, 2, 4, 8, and 16 pounds per tree. At that time the trees showed an average level of 0.49 microgram of extractable boron per 10 sq. cm. of foliage. Heavy rains commencing June 18 aided uptake of boron to the extent that on June 26 foliage samples from the above rates of application showed, respectively, 1.10, 1.16, 1.56, 1.64, 2.08, 2.32, and 3.08 micrograms of boron per 10 sq. cm. This precise delineation was regarded as excellent preliminary proof of the method. Analyses from these trees were made at frequent intervals and the entire data published (1). Analyses from late summer samplings are presented in Table III. Fairly wide variation in the soil beneath these trees is reflected in rate of leaching and in uptake—for example, the soil under tree 13 permitted a high rate of leaching loss but also a high

Figure 4. Sampling Knife

rate of uptake. This study has revealed a wide spread between normal and toxic levels of boron in pecan foliage, normal foliage containing about 2 micrograms of extractable boron per 10 sq. cm., while all foliage developing toxic symptoms (marginal burn) contained 17 micrograms or higher.

While the increments in rate of borax application in the lower values seem small, each actually is 100% greater than the one before it. The higher values represent applications of several hundred pounds per acre. There still was some question as to whether the foliage extraction method would detect the slight differences resulting from as little as an ordinary economic application (for vegetables) of 10 pounds per acre, or the even smaller differences where an application of 10 pounds of borax (only 1.13 pound of boron) might be influenced in plant uptake by such incidental factors as variation in soil reaction (pH).

Table IV. Influence of Extraction Time on Amount of Boron Extracted, Using Collard Leaves Grown at Various Levels of Soil Boron

(Reported as micrograms of boron per determination—i.e., from eight foliage strips or 5 sq. cm.)[a]

Borax, Lb. per Acre	Extraction Time			
	20 min.	30 min.	40 min.	50 min.
0	0.07	0.16	0.18	0.21
10	0.23	0.36	0.45	0.45
20	0.32	0.42	0.49	0.49
40	0.58	0.65	0.68	0.78

[a] Results normally multiplied by 2 for reporting as micrograms of boron per 10 sq. cm. were here allowed to remain as determined, for clarity of presentation.

The need for a method having this sensitivity was encountered in February 1947 for analysis of an index crop so produced on Lakeland fine sand, a soil of very low fertility. All the necessary nutrients were added and collards were grown as the index crop. As this foliage was very different from that of the pecan, it was thought advisable to run a test for duration of the extraction period, rather than accept 30 minutes which had been found most suitable for pecans. Four adjoining foliage strips were cut from each collard leaf and were placed, one each, in the dishes designated for 20-, 30-, 40-, and 50-minute extraction. This system was followed through eight leaves grown with no borax, then in turn with 10, 20, and 40 pounds per acre. The data from this test are presented in Table IV. The extraction rate for all four boron levels is very similar up to 30 minutes, but becomes erratic thereafter. The 20-minute extraction is believed too short for best results with most types of foliage. On the other hand, resolving power is lost in a period longer than 30 minutes and much extraneous material is extracted, which in some instances might be detrimental. The 30-minute extraction appears best from the standpoint of the procedure, and gives excellent correlation with soil applications of borax.

In Table V the single values for the 30-minute extraction period of Table IV are given in comparison with those established by ashing as nearly identical samples as possible, taken from the same set of leaves on the following day. The ashed values show fairly good correlation for the 0-, 10-, and 20-pound applications, but appear somewhat low for the 40-pound application. Agreement between duplicates is good for the low-boron foliage but least exact where the boron content is highest. The portions for ashing were dried at 80° C., then ashed at 450° C. for 8 hours in the same muffle at the same time. All were protected against entrance of foreign materials by use of Speedyvap

covers, the ridges of which gave elevation for free circulation of air. The resulting ash was taken up with 4 ml. of the "extracting" solution by digesting at about 80° C. for 5 minutes, then cooled, and the usual calcium hydroxide solution was added. From that point the determination was run exactly as for the foliage extracts.

The data in Table VI were developed in much the same way as those of Table V, except that this study was planned from the beginning to include ashing in conjunction with the extraction. To this end the four adjoining 2.5-mm. foliage strips from freshly harvested and washed leaves as soon as cut were treated as follows: The first and third strips were placed in dishes for extraction, while the second and fourth were placed in dishes for ashing. In this manner identical samples were obtained, in duplicate, for both methods of analysis. All samples for analysis by ashing were dried at 80° C., then ashed overnight at 445° C. maximum temperature, all in the same muffle. Analysis of the ash was done as reported for Table V. While agreement between duplicates is good in two of the determinations, in the other three it is extremely divergent. These discrepancies are thought to represent the separate effects of several causes, all related to inequalities in ashing. On the other hand, the data from the extraction procedure indicate good quantitative performance and excellent reproducibility. This is also borne out by the well coordinated data of Table IV. The close agreement between duplicates is the more striking in that it results not from duplicate aliquots, but from extraction of two separate portions of original sample. Duplicate extractions of pecan foliage gave essentially the same close agreement in boron values as reported in Table VI for collards.

CONCLUSIONS

While the extraction procedure has proved its value for analysis of orchard and field crops, it is perhaps most suitable for determining the boron levels in plants grown experimentally in pots, cylinders, or pits. As the foliage requirement is for strips only 2.5 mm. wide and 25.0 mm. long, it should be possible to obtain a sample from leaves of almost any size or shape; and the total area required is sufficiently small (5 sq. cm.) for sampling even pot-grown plants without adversely influencing their current growth or ultimate yield, particularly if the sample is composited, a leaf or two from each of several replications. In addition to the crops mentioned, the procedure has been used satisfactorily for analysis of foliage from a number of representative trees, shrubs, flowers, and vegetables.

Table V. Boron Uptake in Collards from Various Soil Applications as Indicated by Foliage Extraction and by Ashing

(Reported as micrograms of boron per determination—i.e., from eight foliage strips or 5 sq. cm.)[a]

Borax, Lb. per Acre	By extraction[b]	Foliage Boron		
		By Ashing		
		1	2	Mean
0	0.16	0.27	0.25	0.26
10	0.36	0.97	1.02	1.00
20	0.42	1.15	1.11	1.13
40	0.65	1.23	1.37	1.30

[a] See footnote, Table IV.
[b] From 30-minute column of Table IV.

Table VI. Influence of Reaction Levels in Lakeland Fine Sand upon Boron Uptake by Collards, as Determined by Extraction from Foliage and by Ashing

(Micrograms of boron from 5 sq. cm. of foliage)[a]

Treatment No.	Pounds per Acre		Soil pH	Foliage Boron					
	Borax	Reaction supplement		By Extraction			By Ashing		
				1	2	Mean	1	2	Mean
11	10	Sulfur 500	4.34	0.31	0.30	0.31	0.85	0.82	0.84
12	10	None	5.44	0.43	0.45	0.44	0.94	0.89	0.92
13	10	Lime 500	5.78	0.41	0.42	0.42	0.81	1.10	0.96
14	10	Lime 1500	5.99	0.50	0.52	0.51	1.03	1.28	1.16
15	10	Lime 4500	6.66	0.35	0.36	0.36	0.86	1.12	0.99

[a] See footnote, Table IV.

The study of zonal deposition of boron (Figure 3) suggests the use of this procedure for investigating the role of boron in plant nutrition, especially for determining translocation rates and tissue concentrations. As a survey procedure it should serve effectively for classifying the boron-supplying power of the various soils of an area, by analysis of a single plant species growing generally upon them.

ACKNOWLEDGMENT

The author is grateful to G. H. Blackmon, horticulturist, Florida Agricultural Experiment Station, for opportunity to cooperate in a study of boron effects in pecans; also to F. B. Smith, chemist, Department of Soils, Gainesville, and B. R. Fudge, associate chemist, Citrus Station, Lake Alfred, for their valuable suggestions in preparation of the manuscript.

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NOTES ON ANALYTICAL PROCEDURES . . .

Mercury Cathode Cell for Rapid Electrolysis

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BY ELECTROLYSIS with the mercury cathode in dilute acid solution some thirty elements may be removed quantitatively from the other elements which, because of their high decomposition potentials, are not deposited in the mercury (6). By thus removing unwanted elements, many existing procedures for determining the remaining elements may be simplified, with a consequent decrease in time and increase in accuracy of the analysis.

The procedure is well known (1, 3, 4, 5, 7, 9), but its application in the analysis of ores and metals would probably be more general if the electrolysis could be conducted more rapidly than is possible with the type of cell normally used. Some special cells have been designed for this purpose (2, 8, 10), but it is believed that the apparatus described here is more adaptable to control and research work and requires much less time for electrolysis.
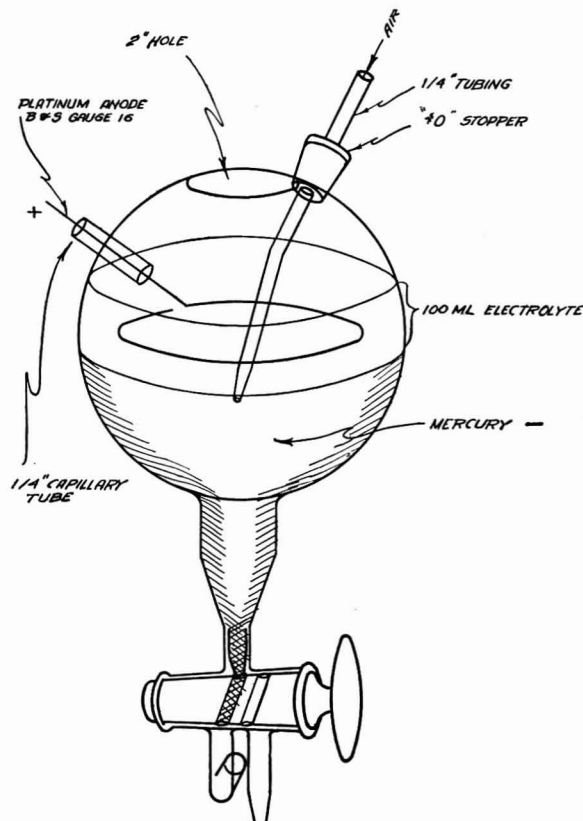
CONSTRUCTION OF CELL

The cell is made from a 700-ml. Pyrex Florence flask modified as shown in Figure 1. It contains about 4 kg. of mercury, which has a surface area of approximately 77 sq. cm. The platinum wire anode has a diameter of about 10 cm. and lies horizontally about 0.5 cm. above the mercury surface. The volume of electrolyte may be from 50 to 100 ml.
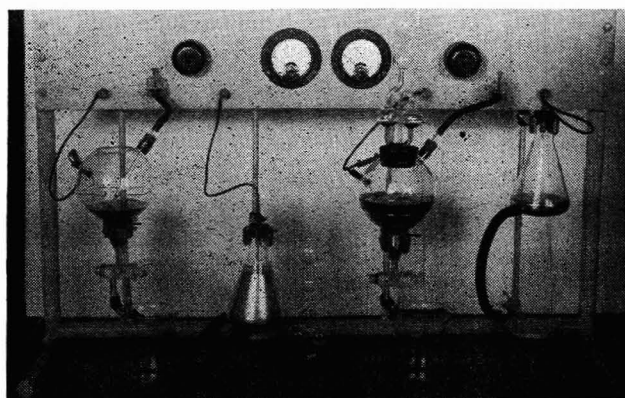

Figure 2.   Two-Cell Assembly

The air-inlet tube is drawn to a fine opening and dips 1 cm. below the center of the mercury surface. A slow current of air is passed through this tube, agitating the mercury and the solution above it. This method of agitation is preferable to mechanical stirring partly because it eliminates possible mechanical failures, but chiefly because it is more effective in continuously exposing a fresh mercury surface to the electrolyte. However, too violent agitation is undesirable, as fine droplets of mercury will form and remain suspended in the acid solution.

A convenient arrangement of a set of two of these cells is illustrated in Figure 2. A larger number of cells can be set up if desired.

During the electrolysis a fine mist forms in the cell and is condensed in the modified thistle tube shown. This tube is supported by a No. 11 rubber stopper which fits snugly into the 5.1-cm. (2-inch) hole in the cell. The U-portion of the tube contains 5 or 6 ml. of distilled water, which readily absorbs the fine spray. A 300-ml. Erlenmeyer flask fitted with an outlet near the base is used as a leveling bottle. Electrical contact with the mercury in the leveling bottle is maintained by a 15-cm. length of platinum wire (B. and S. gage 16), which is held in place by a rubber stopper containing an air vent.

The wiring of the circuit is illustrated in Figure 3. The two cells are connected in series, but the left-hand cell can be cut out
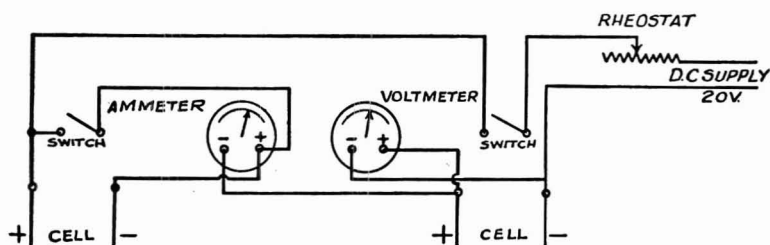

Figure 1.   Modified Mercury Cathode Cell

Figure 3. Wiring Diagram

of the circuit by the snap switch on the panel above it. The switch on the right-hand side controls the main power supply. The whole assembly rests in a shallow tray, so that any mercury spilled accidentally may be recovered.

OPERATION OF CELL

Electrolysis is usually conducted in 0.3 N sulfuric acid solution. The direct current supply is adjusted by a rheostat so that the amperage in each cell is not less than 6 and preferably 7 with a voltage of 5 to 6. Under these conditions most samples are electrolyzed completely in 30 to 40 minutes. After testing for the complete removal of the unwanted elements, the leveling bottle is lowered and, as soon as the mercury has drained from the cell, the electrolyzed solution is run into a 400-ml. beaker. The thistle tube and cell are rinsed with water and the rinsings are added to the beaker. If the solution contains some fine, blackish suspension (arsenic, manganese, etc.), filter pulp is added and the mixture is filtered on a No. 30 Whatman paper. Meanwhile, about 30 ml. of 2% sulfuric acid are added to the cell, the leveling bottle is raised, and electrolysis is continued for 5 minutes.. This is a precautionary measure to ensure recovery of any electrolyte entrained with the mercury in the rubber tube. This wash solution is then run off, the thistle tube and cell are rinsed with distilled water as before, and the combined washings are filtered through the original paper.

In Figure 2 the right-hand cell is in the position for electrolysis, while in the left-hand cell the electrolyzed solution has been separated from the mercury and is ready to be drawn off.

If the original sample is large and contains much iron, it is desirable to add a little ammonium hydroxide to neutralize the acid formed during electrolysis. Addition of ammonium hydroxide is usually indicated if the solution is not colorless after 20 minutes' passage of the current.

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Phosphoric Acid Attack Method for Determination of Silicon in Aluminum Alloys

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RECENTLY Lisan and Katz (1) described a rapid phosphoric acid attack method for the determination of silicon in aluminum alloys. To improve the accuracy of this method this author suggests: (1) the use of casseroles instead of beakers in order to eliminate the considerable error that can be caused by the dissolution of the glass by the phosphoric acid, if the beakers are kept on the hot plate more than 2 minutes past the point at which the elemental silicon dissolves, and (2) the use of a lower temperature (900° C.) and shorter ignition period (10 minutes) for the ignition that follows the treatment with hydrofluoric acid. The recommendation of Lisan and Katz that this ignition period be at 1100° C. to constant weight can lead to high results, because of the slow volatilization of phosphoric acid (2).

RECOMMENDED PROCEDURE

Weigh the sample in a 500-ml. casserole:

        2 grams, 1.5 to 4.5% silicon
        1 gram, 4.5 to 10% silicon
        0.5 gram, over 10% silicon

Add 80 ml. of acid mixture (made by mixing 750 ml. of phosphoric acid, 1000 ml. of nitric acid, and 250 ml. of sulfuric acid) to the 1- or 2-gram samples, or 60 ml. of acid mixture to the 0.5-gram samples. Cover with a watch glass and warm on the hot plate until the sample is completely in solution. (If the sample is very finely divided, allow the initial reaction to subside before heating.) Remove the watch glass and evaporate until the solu-

tion clears. The end point is not critical, and the casserole may be kept on the hot plate indefinitely. Add a pinch of ammonium nitrate, swirl, and remove from the hot plate. Allow the solution to cool somewhat, add 60 ml. of 70% perchloric acid, and evaporate to strong fumes of perchloric acid. Cover with a watch glass and fume strongly for 8 to 10 minutes. Remove the casserole from the hot plate and allow to cool somewhat. Add 300 ml. of hot water and 40 ml. of hot gelatin solution (1%), and stir well. Filter through an 11-cm. No. 41 Whatman filter paper containing paper pulp. Swab the casserole, and wash the precipitate 12 times with hot dilute sulfuric acid (1%) and finally a few times with hot water. Transfer the paper and precipitate to a clean platinum crucible and char off the paper carefully. Ignite the silica at 1100° to 1200° C. to constant weight (for routine work 35 minutes are ample). Add 3 drops of dilute sulfuric acid (1 to 1) and 5 ml. of 48% hydrofluoric acid, and evaporate carefully to dryness. Ignite at about 900° C. for 10 minutes. The difference in the two weights represents silica. The factor for converting silica to silicon is 0.4672.

The phosphoric acid attack method is not recommended for the analysis of aluminum alloys containing less than 1.5% silicon (1).

Results obtained for the above procedure averaged 0.02% higher than the results obtained for the alkali-attack single-dehydration method.

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Preparation of Silver for Use in Walden Silver Reductor

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SILVER for use as reducing agent in the Walden silver reductor (1) is usually prepared by the displacement of silver from a slightly acidified, concentrated solution of silver nitrate by the action of copper in the form of heavy sheet or large-gage wire.

In the authors' hands, silver prepared in this manner has been so finely divided that the flow of solution through the reductor is too slow or the operation requires reduced pressure. The flow is further retarded by the deposition of silver chloride and regeneration is difficult. The method described here for the preparation of silver reductor metal eliminates these difficulties. The process involves preparation of electrodeposited silver under conditions which result in "silver tree" type aggregates, minute yet distinctly granular, brilliantly reflecting crystals, of low apparent density with a high ratio of surface to mass.

Electrodeposition of Silver as Tree Silver. The electrolyte consisted of about 500 grams of silver nitrate dissolved in 2500 ml. of water, slightly acidified by the addition of nitric acid and contained in a 4-liter beaker. The cathodes were of heavy-gage platinum with heavy "lead in" conductor extensions. Each of two cathodes was 10 cm. square and was suspended in the electrolyte by use of heavy copper bus bar connections to a source of direct current. The anode was either a silver rod 10 to 25 mm. in diameter and 200 mm. long or a similar amount of silver as a heavy-gage rectangular sheet, in either case suspended in the center of the silver nitrate electrolyte with the platinum cathodes placed at the outer edges of the deposition cell.

A current of 60 to 70 amperes at a voltage of 5 to 6 volts served to deposit the silver in the proper form. This electrical energy is best supplied by use of a motor generator set. The electrolyte need not be stirred or cooled. The silver deposits in mosslike, multibranched, brilliantly refracting crystals of silver in the four outside edges of the platinum cathodes, from which it may be dislodged by gentle tapping. About 30 grams of the silver in this form occupy a volume of 40 to 50 ml. or sufficient for one correctly designed Walden reductor tube.

Preparation of Walden Reductor Apparatus. A reductor column of the usual Jones reductor type (1) held a sufficient quantity of silver preparation for satisfactory operation. The silver was introduced into the tube above a small plug of glass wool and then compressed within the tube as it was inserted (a blunt-ended ramrod device was used) to as great an extent as required without restricting the free flow of solution through the column.

Reductor Performance. A molar solution of hydrochloric acid was prepared which contained 0.1 mole of ferric chloride. The reductor was rinsed, using molar hydrochloric acid, and tested starting with the reductor filled to the top of the silver with molar hydrochloric acid. The top reservoir was filled with the ferric chloride solution and the lower stopcock opened fully. The solution to be reduced was continuously passed through the reductor until it was no longer quantitatively reduced. Four hundred milliliters of the 0.1 molar ferric chloride were reduced in 5 minutes of flow. This amount of reduction would account for the quantity of iron to be reduced in 12 to 15 ordinary analyses. The reductor is completely rinsed in an actual quantitative determination by the passage of 100 ml. of molar hydrochloric acid in 5 equal portions, each consecutive portion being allowed to pass through the reductor down to the level of the silver.

Reductor Regeneration. To free the silver from deposited silver chloride, it is rinsed with water and filled completely with dilute 1 to 3 reagent ammonium hydroxide. The silver chloride is removed completely from the silver by this treatment and may be rinsed out of the reductor tube with water followed by molar hydrochloric acid and is then ready for re-use. It is always advisable to allow the dilute ammonia to stay in contact with the silver for 5 to 10 minutes before rinsing it from the reductor, although the solution of the coating of silver chloride seems to be removed instantly. The regenerated reductor performs in every way precisely as indicated, no matter how many times it is regenerated. As a precautionary measure the ammoniacal solution of silver chloride should be promptly discarded or acidified.

The procedure described requires special equipment for its preparation, such as large silver anodes and platinum cathodes together with a source of low voltage–high amperage direct current. For this reason silver of suitable form should be ultimately supplied through regular trade channels. The reductor, because of its limited quantity of silver and its abnormally small apparent density, requires more frequent regeneration. These limitations are far outweighed by the resultant advantages.

LITERATURE CITED

(1) Walden, Hammett, and Edmonds, *J. Am. Chem. Soc.*, 56, 350 (1934).

Book Reviews

Volumetric Analysis. Titration Methods. Acid-Base, Precipitation and Complex-Formation Reactions. *I. M. Kolthoff* and *V. A. Stenger.* Volume II. Second revised edition. xiii + 374 pages. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y., 1947. Price, $6.00.

This volume of the second edition covers the practical aspects of volumetric titrations except for oxidation-reduction reactions, which are to be included in Volume III scheduled for publication in late 1948. (Volume I of this revised series, published in 1942, covered the theoretical fundamentals.) Revision has been thorough. Many new methods, modifications, and recent references are included.

Volume II is divided into three main parts: (A) Apparatus and General Principles, (B) Acid-Base Reactions, and (C) Quantitative Precipitation and Complex-Formation Reactions. Part A contains many practical pointers about the calibration and use of volumetric apparatus of all types and the selection of primary and secondary standards. Numerous tables useful in calibrating glassware are included.

Part B describes the indicators and primary standards available for acid-base reactions and then considers a large number of actual examples of acid-base titrations including displacement titrations, hydrolytic precipitations, and special methods. Procedures and notes describing variations in procedure, interferences, and applications are given for most of the examples.

Part C consists of a large chapter on argentometric procedures and two smaller chapters on mercurimetry and other precipitation methods. As in Part B, the indicators, primary and secondary standards, and procedures are adequately described and annotated.

The authors have not intended to cover exhaustively all applications of volumetric analysis. They have given a broad selection of useful and reliable methods, trying to emphasize the fundamental principles involved. Nevertheless, the reader will find within this volume examples of determinations of substances of interest to all fields of pure and applied chemistry.

Emphasis has been placed upon the attainment of the highest possible precision in the methods described in the volume. The reader can then determine for himself the refinements necessary for his particular problem. The authors have apparently tried out most of the procedures themselves, and have given many valuable comparisons of the relative merits of the methods.

Only a very few minor and obvious errors in typography were noted, except that the last equation on page 27 and the equation given in the illustration on the next page should read $+C_t$ rather than $-C_t$ if C_t has the signs as given in the table on page 22. The binding is good and the paper about average.

This reviewer would not hesitate to recommend this book to anyone interested in the practice of volumetric analysis and hopes that the third volume will not be long delayed. LYNNE L. MERRITT, JR.

Symposium on Modern Methods of Analytical Chemistry

L. T. HALLETT, Associate Editor

A COMPREHENSIVE review of the techniques and tools of present-day analytical methods by 12 experts featured the meeting held at Louisiana State University February 2 to 5. The symposium, organized by Philip W. West of the Department of Chemistry and Physics, attracted 200 from the southwest and other states. Besides the formal presentations, the two informal round table discussions in the evening brought out the fact that research in analysis by competent analytical personnel is becoming increasingly important. The analyst may be chemist, physical chemist, or physicist, depending upon the tools employed.

Modern analysis requires the technician without formal college training to collect data and carry out routine, repetitious analysis, using well-designed instruments. It is the function of the research analyst to interpret and correlate data and direct research on new methods. That such men should work as consultants an form part of the research team in the solution of problems was recognized as desirable and necessary.

H. A. Laitinen, University of Illinois, covered the principles, theory, and application of the polarograph. The use of this method in inorganic analysis is well established, but its use in the study of organic systems is a relatively new field in which those with a good training in organic chemistry must pioneer.

He said that the use of the polarograph for amperometric titrations is being extended. A simple apparatus can be built for this method and it has the advantage over the potentiometric method that it can be carried out more rapidly, and also a suitable voltage can be selected best fitted for the system under study.

Philip W. West, in his paper on noninstrumental methods of of analysis, dealt briefly with chromatography of colored and noncolored systems, partition-chromatography, and quantitative spot tests which are a method of applied chromatography. The use of complex ion formation to prevent interferences, to form distinctive products for colorimetric analysis, and in the establishment of desired formal potentials for electrometric methods was discussed. The importance of organic reagents, catalytic reactions, and bioassays in analysis was covered. The reduction of methylene blue in the presence of selenium or its compounds is a strikingly simple but specific method for this element.

Arthur L. Le Rosen, L.S.U., covered in some detail the need for standardization of chromatographic adsorbents and the demand by all those using this method for more fundamental knowledge. In the analytical applications better adsorbents are required. Its value in qualitative as well as quantitative organic analysis was stressed.

Philip J. Elving, Purdue University, and chairman of the A.C.S. Division of Analytical and Micro Chemistry, discussed the most significant developments in analytical chemistry during the past quarter century. He pointed out that the trends during that period prove conclusively that analytical chemistry covers a wide field, which will necessitate changes in the teaching of this subject. The role of the analyst is a complex one, demanding a wide knowledge of science in general, together with specialization in some particular branch of his interest and aptitude.

METHODS FOR ANALYSIS OF LIGHT HYDROCARBONS

C. E. Starr, Jr., Esso Laboratories, Baton Rouge, La., discussed the evaluation of analytical methods employed in the control and assay of feed stocks and product involved in the production of butadiene, and the comprehensive test programs conducted by the Butadiene Committee on Specifications and Methods of Analysis for this purpose. This committee was organized under the sponsorship of the Reconstruction Finance Corporation's Office of Rubber Reserve and was composed of members of that government agency and of industrial concerns which were feed stock suppliers or producers of butadiene.

A number of synthetic mixtures of hydrocarbons were prepared by the Phillips Petroleum Company and were analyzed by the cooperating members of the committee to determine how well a given laboratory checks its own analyses, how well various laboratories check each other, how precisely and accurately the various gas components are determined, and the most suitable analytical methods.

Analytical methods employed in the test program included low-temperature distillation, infrared and ultraviolet absorption spectrometry, various chemical tests, and mass spectrometry. Analysis of over 8000 test results is in progress, and the preliminary conclusions are as follows: Individual laboratories were found to be able to check their own analyses, by any of the standard methods employed, with excellent precision. On the average, a given laboratory can be expected to make determinations for most light hydrocarbon components of a gas with a probable error of ± 0.2 to 0.3 mole %.

The extent to which laboratories check each other is within values two-to three times the probable error for a given laboratory. Each of the standard methods employed was found to have unique advantage with respect to accuracy and precision of measurement. The mass spectrometer method appears best for determination of individual paraffin hydrocarbons, total butenes, and butadiene in high concentrations. The ultraviolet absorption spectra method is advantageous for butadiene in low concentrations. Infrared absorption spectra measurements are best for isobutylene and individual n-butenes. Distillation and mass spectrometer methods show about the same accuracy and precision for total C_3, total C_4, and total C_5. Chemical methods show little, if any, advantage for specific olefin hydrocarbons.

In general, methods are available for determination of the main light hydrocarbon components with an accuracy of 0.3 mole % and a precision of 0.25 mole % (expressed as probable error).

Methods developed and tested will be described along with detailed test data in a book on light hydrocarbon analysis to be published by the Office of Rubber Reserve. Editors are O. W. Burke of Rubber Reserve, F. D. Tuemmler of Shell Development, and Dr. Starr. An enlargement of test material summing the Rubber Reserve analytical test program will soon be offered for publication in ANALYTICAL CHEMISTRY.

GENERAL APPLICATIONS OF MASS SPECTROMETRY

General applications of mass spectrometry was the subject of B. W. Thomas of the Humble Oil and Refining Co.:

During the past two years mass spectrometers of the type manufactured by Consolidated Engineering Corporation and Westinghouse have been put into operation in the laboratories of the Baytown Humble Oil and Refining Company. Over 17,000 runs, including more than 12,000 analyses, have been performed on these instruments. Calibration data have been measured for over 145 pure gaseous and liquid compounds boiling up to 330° F. Although a major portion of the samples analyzed have been of a routine nature, considerable effort has been directed toward the development of specialized techniques including (1) extension of mass spectrometer analyses to higher molecular weight hydrocarbons and other type compounds through use of high-temperature operations and internal standards, (2) use of a low-temperature fractional condensation unit for concentration of trace components, and (3) rearrangement of the mass tube and electrical circuits to permit measurement of negative ions. This paper discussed data from these applications of mass spectrometry.

Analyses were shown for five gaseous samples to illustrate the accuracy and reproducibility obtainable on mixtures of this type. These results included determination of paraffins, olefins, and acetylenes in the C_1 to C_5 range, carbon dioxide, carbon monoxide, oxygen, nitrogen, and hydrogen.

Trace component analyses were shown for a synthetic mixture in which the concentrations of C_2 to C_5 paraffins were very small in comparison with the concentration of methane. The analyses also included determinations for carbon dioxide, carbon monoxide, and nitrogen, hydrogen, and helium. A special low-temperature fractional condensation unit in this type analysis was described.

Results were shown for four liquid samples which indicate

applications of the mass spectrometers to two typical plant control streams. The data included analyses of two synthetic mixtures simulating a cyclohexane concentrate stream containing benzene, n-hexane, two C_6 naphthenes, and six C_7 paraffins, and an aromatic stream containing C_8 to C_9 aromatics admixed with paraffins and naphthenes. Liquid sample introduction procedures, high-temperature operation of the mass spectrometer tube and vacuum system, and the use of an internal standard for materials of high molecular weight were discussed.

The production of negative ions by electron bombardment in the mass spectrometer and electrical circuit changes required for their detection and measurement was discussed. Negative and positive ion abundance data and electron energies required for their production were shown for several compounds.

L. T. Hallett, General Aniline and Film Corp., discussed the type of personnel, organization, and training required in the solution of analytical problems. The importance of the integration of chemical research with research analysis was shown. Typical problems and methods for their solution were outlined, with emphasis on why false results can be obtained if a limited approach is used. The necessity of pure standards was considered, together with the limitations of elementary analysis. Microtechniques were shown to be necessary in the solution of many analytical problems.

Dr. Müller, in his column "Instrumentation," covers the instrumental aspects of the conference.

THE ANALYST'S CALENDAR

Modern Instrumental Methods of Analysis

A tentative program has been prepared for the Symposium on Modern Instrumental Methods of Analysis, which is to be given under the sponsorship of the Minnesota Section of the American Chemical Society and the Institute of Technology, University of Minnesota, at the Center for Continuation Study.

Monday, March 22

General Instrumentation Methods. Ralph H. Müller.
General Optical Methods. E. J. Meehan.
Molecular Weight Determination by Light Scattering. P. Debye.
Infrared Absorption Spectrometry. R. B. Barnes.
Raman Spectra. E. J. Rosenbaum.
Analytical Applications of Electron Microscopy. J. Hillier.

Tuesday, March 23

Use of Visible and Ultraviolet Spectra in Analysis and Identification. R. N. Jones
Polarography and Amperometric Titrations. I. M. Kolthoff.
Mass Spectroscopic Methods. A. O. C. Nier.
Analysis by Emission Spectroscopy. J. R. Churchill.
X-Ray Methods of Analysis. L. K. Frevel.

Wednesday, March 24

Radioactive Tracers as an Analytical Tool. P. R. O'Connor.
Analytical Applications of Molecular Distillations. E. S. Perry.

Developing New Analytical Test Methods

The Division of Analytical and Micro Chemistry is planning a Symposium on the Design of Experiments for Developing New Analytical Test Methods for presentation at the Chicago meeting of the American Chemical Society in April. The tentative program includes the following papers:

Introduction. Grant Wernimont, Eastman Kodak Co.
Design of Simple Experiments. John C. Hintermaier, Vanity Fair Mills, Inc.
Statistical Tests of Significance. J. H. Davidson, Merck & Co., Inc.
Multiple Factor Experiments.. W. J. Youden, Boyce Thompson Institute for Plant Research.

Beginning Course in Quantitative Analysis

A tentative program has been arranged for the Symposium on Contents of the Beginning Course in Quantitative Analysis, sponsored by the Divisions of Analytical and Micro Chemistry and of Chemical Education, which is to be held in Chicago during the spring meeting of the American Chemical Society. The final program will be printed in Chemical and Engineering News for March 15.

Introduction. Philip J. Elving, Purdue University.
Quantitative Analysis for Premedical Students. Olaf Bergeim, University of Illinois College of Medicine.
Quantitative Analysis for Undergraduate Chemistry Majors. George Calingaert, Ethyl Corp.
Quantitative Analysis for Home Economics Students. Martha Johnson, General Electric Co.
Quantitative Analysis for Chemical Engineering Students. Odon S. Knight, Commercial Solvents Corp.
Teaching Quantitative Analysis to Large Groups of Students. William MacNevin, Ohio State University.
Discussion of the Content and Teaching of the Beginning Course in Quantitative Analysis. N. Howell Furman, Princeton University; Edward L. Haenisch, Villanova College; William T. Hall, Rochester, Mass.; I. M. Kolthoff, University of Minnesota; Harold M. State, Allegheny College; Philip W. West, Louisiana State University.

International Congress on Analytical Chemistry

Under the auspices of the Netherlands Chemical Society an International Congress on Analytical Chemistry will be held at Utrecht, Holland, June 1 to 3. Papers will be presented in sections on general methods and standardization, electrical methods, emission spectrography, optical methods and chromatography, and microbiological methods and traces. Preprints will be distributed before the meeting, and papers will be published in Analytica Chimica Acta and Spectrochimica Acta.

Among those presenting papers will be G. Charlot, G. Duyckaerts, W. J. Gooderham, I. Heyrovský, E. Leclerc, E. Loeuille, H. W. Thompson, P. E. Wenger, and Trevor I. Williams.

C. J. van Nieuwenburg is chairman of the organizing committee, and H. A. J. Pieters, Beatrixlaan 7, Geleen, Holland, is secretary.

Third Annual Symposium. Metropolitan Microchemical Society of New York, Feb. 27 and 28.
Symposium on Modern Instrumental Methods of Analysis. Minnesota Section, A.C.S., and Institute of Technology, University of Minnesota, Minneapolis, March 22 to 24.
American Society for X-Ray and Electron Diffraction, joint with Crystallographic Society of America, Yale University, New Haven, Conn., April 1 to 3.
Symposium on Analytical Methods in Nuclear Chemistry. Division of Analytical and Micro Chemistry, Northwestern University, Evanston, Ill., Aug. 13 and 14.

Rapid Precipitate Dryer and Solvent Evaporator. Irving R. Hunter, Western Regional Research Laboratory, Albany, Calif.

FOR drying solids or evaporating solutions, the apparatus illustrated has been found effective and time-saving. The dryer consists of two Pyrex funnels of Büchner type, with fritted disks, to each of which is sealed a ground-glass joint provided with glass hooks. The drawing illustrates an apparatus in which standard-taper 24/40 joints have been sealed to funnels containing disks 30 mm. in diameter. Porosity of the disks should be coarse or medium.

The sample is placed (or filtered) in the funnel equipped with outer joint. In most cases, the funnel should not be more than two thirds full of wet solid at the start. The apparatus is closed and the joint is held in place with rubber bands. A slow stream of air (or inert gas, if required) is allowed to pass upward through the precipitate for a few minutes. If lumps tend to form, they should be broken up with a rubber policeman. Thereafter, the funnels are soon filled with an agitated mass of particles which are quickly dried. Most of the common solvents are completely removed in 5 to 15 minutes. In the case of colloidal precipitates, or if high-boiling solvents are present, longer periods may be required.

Larger apparatus made from funnels up to 90 mm. in diameter have been used for drying bulk precipitates and for evaporating solutions. In the case of the latter, a slow stream of air is first allowed to pass through the lower funnel. The solution is then added, the apparatus is closed, and the air stream is increased until a lively boiling effect is obtained. Application of a source of vacuum to the outlet may be used to increase the rate of evaporation.

AIR

Figure 1

A Simple Mechanical Pipet Filler. David B. Brinton, Utah State Department of Health, Salt Lake City, Utah.

PRACTICALLY every analytical laboratory worker has occasion to pipet liquids which give off obnoxious and dangerous fumes. These fumes range from annoyances such as chloroform to deadly poisons such as tetraethyllead. These workers are well aware of the undesirability of drawing into their mouths liquids which it is desirable to measure volumetrically with a pipet; the health hazards have been recognized and become a source of concern to laboratory supervisors throughout industry. One large chemical company has set up a safety rule which forbids the use of the mouth for pipetting under any condition.

There are on the market several suction devices which have been designed to operate with a pipet. In several different laboratories, the author has introduced the pipet sucker here illustrated. One application

SUCTION

RUBBER STOPPER

PIPET
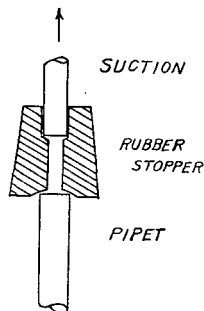
covered the sampling of hot 20% hydrochloric acid pickling solution and another was in the sampling of high-octane gasoline which contained appreciable quantities of tetraethyllead.

An ordinary water pressure aspirator is connected with a convenient length of laboratory rubber tubing to a small piece of glass tube, 2 or 3 inches long, the end of which penetrates approximately half-way through a No. 4, 1-hole rubber stopper. The open end of the rubber stopper is countersunk to form the lip contact for the pipet. The countersinking can be easily and efficiently done by gently, but firmly, reaming the hole with a 0.5-inch high-speed drill. The hole which results is smooth and soft and makes an air-tight seal when there is only a slight pressure applied with the pipet. If it is desirable to have both hands free, the rubber stopper can be mounted in a buret clamp on a ring stand.

Adjustment of the water flow through the aspirator will regulate the suction for either fast or slow filling of the pipet.

Constant-Level Control for Water Baths. Chester A. Snell, Foster D. Snell, Inc., 29 West 15th St., New York 11, N. Y.

A DEVICE employed in these laboratories for some time enables use of practically any container as a constant-level water bath. It has not been described previously in the literature, but the author does not know exactly where the idea originated.

The diagram is largely self-explanatory. None of the dimensions are critical. For large water baths 35-mm. tubing is used for the outside tube and 7-mm. tubing for the water and siphon
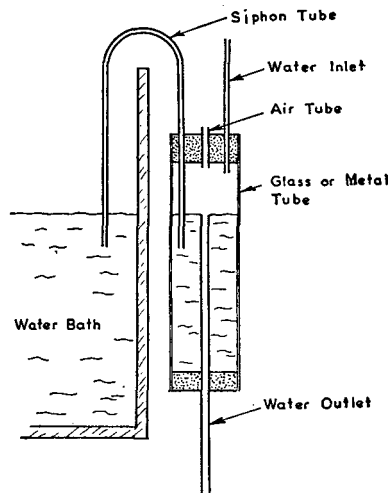
tubes. The third tube in the upper stopper opens to the air to prevent air locks in the controller. To operate the device it is hung on the side of the water bath with the water-outlet tube adjusted to the height of water desired in the bath. The air tube and water outlet are closed and water is run in through the water-inlet tube until the siphon tube is filled. The air tube and water outlet are opened and the rate of water-flow into the device is adjusted to give a slight continuous overflow into the outlet tube.

If a few of these controllers are kept on hand, it is possible to make a constant-level water bath in a few minutes by using any convenient container such as a beaker or pail.