



ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

The Pratt Trace Analysis Laboratory

SCIENTISTS for years have been very much aware of the importance of the so-called trace elements to life and industry. It is somewhat amazing, however, to find an individual with sufficient interest in and knowledge of this specialized field to donate a very sizable sum (\$125,000) for fundamental research in analytical methods for the detection and measurement of trace elements. Our amazement (but not our enthusiasm) was tempered somewhat when we learned that the donor, John Lee Pratt, is a graduate of the engineering school of the University of Virginia and in his various industrial activities and associations has maintained a lively interest in science.

Whether a plant, or an animal, or even a human being, lives and thrives, or withers and dies, depends upon the presence of one or more chemical elements in such minute quantities as frequently to defy detection even by modern methods of analysis. Many industrial processes likewise depend upon the presence of very small quantities of elements, and separation and identification often baffle the analyst. It has been pointed out that 55 of the elements occur only as trace quantities and despite our great strides in pushing back the frontiers of chemical knowledge we really know very little about the properties of many elements.

Several, including cobalt, copper, and zinc, are known to be essential to the healthy growth of some organisms but in such small quantities that it is only in recent years and with the advent of new analytical tools of research that this fundamental information has been made available by the analyst to researchers. Thanks to our slowly increasing knowledge of trace elements we are solving, for example, age-old problems concerned with crop failures and unhealthy cattle, but as yet we have not done much more than scratch the surface in exploring the significance of trace elements in most fields of physical science.

How little we really did know about detecting and determining quantitatively very small quantities of many of the elements was dramatically brought home to us as we moved into high gear in the Manhattan Engineer Project. The story of how the research analyst overcame one bottleneck after the other in the atomic energy program was most interestingly disclosed by Professor Furman of Princeton University in his Fisher Award Address last year. As scientists delve further into the innermost secrets of nature, obviously the analytical chemist will be called upon to devise many new swift, sensitive, and accurate methods of analysis.

The Pratt fund not only will provide special apparatus and instruments, but also is to be used to finance over a six-year period several research fellowships in analytical chemistry, especially in colorimetric analysis and other techniques employed in the determination of minute amounts of chemical

elements. Two large laboratories and a darkroom for photographic work have been assigned the new activity. Colorimetric analysis will be conducted in one room; the other will contain the latest and most modern equipment for spectrographic analysis.

The John Lee Pratt Trace Analysis Laboratory at the University of Virginia is under the direction of John H. Yoe, who has been professor of chemistry since 1919 and is widely known nationally and internationally for his fundamental researches in analytical chemistry. The gift by Mr. Pratt which has made possible the new laboratory and several research fellowships is more than a personal tribute to John Yoe. It is one more indication and a very significant one that analytical chemistry is gaining the public attention and recognition it so richly deserves.

Kolthoff — Nichols Medalist

THE profession of analytical chemistry was signally honored this month when I. M. Kolthoff of the University of Minnesota received the Nichols Medal of the New York Section of the AMERICAN CHEMICAL SOCIETY. Dr. Kolthoff's long and fruitful career in chemistry has been devoted largely to fundamental research in analytical chemistry.

It is not our intention here to review in detail Dr. Kolthoff's acceptance address. Purposely we are publishing it in full in the March 21 issue of *Chemical and Engineering News*, so as to bring a number of pertinent statements made by the medalist not only to the attention of his associates in the field of analytical chemistry, but to those in managerial and executive positions in industry, and in our colleges and universities. His authoritative description of the vital role of analytical chemistry in modern research created a most favorable impression on his audience in New York. We are confident the much larger audience provided by *Chemical and Engineering News* will react in a similar manner.

Reprints of Annual Reviews

ATTENTION of our readers is called to the availability of combined reprints of the reviews published in the January and February issues at \$1.50 per copy. Orders should be sent to the Reprint Department, AMERICAN CHEMICAL SOCIETY, 1155 Sixteenth St., N.W., Washington 6, D. C.

The reviews will be continued. A few subjects covered this year will be omitted in 1950; others will be added. We welcome constructive suggestions and criticisms. To the large group of authors who made our initial reviews such outstanding successes, we extend our thanks. We are happy to report that, with but one or two exceptions, the authors have enthusiastically agreed to continue their cooperation another year.

Nucleonics and Analytical Chemistry Symposium

The following seven papers were presented at the First Annual Summer Symposium on Analytical Chemistry, Northwestern University, Evanston, Ill., August 13 and 14, 1948, under the sponsorship of the Division of Analytical and Micro Chemistry and ANALYTICAL CHEMISTRY

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Radioactive Isotopes as Tracers

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Radioisotopes are probably not true tracers in experiments which involve diffusionlike processes, especially when tracers for the lighter elements are being employed. They are probably not true tracers in many common reactions that cannot be forced to essential completion, or in reactions that involve the reaction of only one of two symmetrical functional groups. In all cases careful consideration of the experiments to be performed will allow correct evaluation of experimental data with regard to the possibility that isotope effects are exerting unusual influence on the results.

IN THE past decade there has been great progress in the application to analytical problems of all kinds of the tool afforded by radioactive (and stable) isotopes. The recent very rapid advances in the field have attracted a large number of new investigators, and it is to be expected that many mistakes made ten years ago are being repeated on a grand scale today. Recent fundamental research has shed light upon several problems which makes it necessary to re-examine the entire aspect of analytical use of radioisotopes with some care. This paper points out some of the difficulties, the traps and pitfalls, which await the unsuspecting. Some applications of the method are discussed, but only in so far as is necessary for elucidation of a given problem.

A detectable isotope of a particular element is useful in that its physical and chemical behavior is essentially that of the "normal mixture" of stable isotopes. The word "essentially" is an important one, because this identity of properties may or may not be complete. In fact, one can divide "tracers" or "tags" into two classes on this basis.

In many situations, radioactive isotopes of an element behave as true tracers for the atoms of the element in question—i.e., they are spies (δ) whose presence, within experimental error, is undetectable until they betray themselves by disintegration. It is possible to say with some certainty that this kind of behavior is the rule where the stable isotopes and the isotopic label do not differ by a large fraction in mass, and where processes involving establishment of a small number of consecutive equilibria are involved. Classification in this group is dependent, at least in part, upon the precision with which measurements can be made, as well as upon the factors mentioned immediately above.

In other circumstances radioactive isotopes act as near-tracers or tagged atoms which differ somewhat from the normal mixture of stable isotopes in their properties, but are often acceptable labels for the elements in question. Actually this is a statement of general fact rather than a description of a certain class of nuclides, for all behavior patterns can be contained therein by the assumption of a scale of degree to the exclusion of considerations of kind. Ordinarily, reverting to the statement as a particular rather than a general one, this classification embraces all stable-

unstable pairs whose behaviors differ to such an extent that the chemical or physical processes involved in a particular application can distinguish or discriminate between the isotopes. This effect is observed where the ratio of mass numbers of the isotopes in question differs markedly from unity, where many (successive) equilibria are established, or where reactions are observed in the essential absence of the corresponding reverse process.

Several examples of extreme behavior suggest themselves immediately: Tritium, with a mass of approximately 3, is, for many purposes, practically a different element from ordinary hydrogen, because of the tremendous mass ratio; distillationlike processes involve the establishment of many successive equilibrium states, thus magnifying even very small differences in isotopic behavior, though the effect of such differences is eliminated if the distillation is carried to completion and all distillate fractions are mixed; diffusion processes operate in the absence (practically) of the reverse phenomenon and are able to accentuate differences in isotopes, a good example being the large-scale thermal diffusion separators now in operation. Before discussion of these isotope effects, it may be profitable to take up some matters of analytical technique.

ISOTOPE DILUTION ANALYSIS

Many applications of radioactivity involve analysis of more or less complex mixtures. When a multicomponent system is to be analyzed for one of its constituents, and especially when the properties of several of these components are very similar, the purification of any one fraction is a delicate and tedious process. In general it will be impossible to determine the desired constituent quantitatively because purity and recovery under these conditions are mutually exclusive. This determination can, however, be accomplished through the agency of tracers (3, 6, 11, 15, 16, 18).

Consider a situation in which a radioactive isotope is to be used as a tracer (in many situations stable tracer preparations are just as conveniently employed, but the computation of results is somewhat more difficult). Let a quantity of the component for which analysis is to be made be synthesized containing the radioactive isotope in some stable part of the molecule.

Suppose, further, that a milligrams of the tracer material having a specific activity of A counts per minute per milligram are added to the crude sample; the total activity added is aA counts per minute. The unlabeled compound, that substance for which the analysis is being made, serves as inactive diluting material. If there are b milligrams of this inactive substance, then there will be a plus b milligrams total of the compound in the mixture. Now the mixed sample is carefully analyzed for the desired component, a very small amount being isolated. Let us call the specific activity of this final sample C counts per minute per milligram. The total amount of activity added was aA counts per minute, and clearly it is also equal to $(a + b)C$ counts per minute. The ratio of the initial and final specific activities is given by the relation

$$\frac{\text{Specific activity of tracer}}{\text{Specific activity of total sample}} = \frac{aA/a}{aA/(a+b)} = \frac{(a+b)}{a}$$

In this example b is the desired quantity. If the ratio of the specific activities is called Z , then

$$b = a(Z - 1)$$

The only requirements to be met are that an amount of pure compound sufficient for radioactivity analysis must be isolated successfully, and that the label be located in an unreactive position. It is possible to analyze a multicomponent mixture for several compounds simultaneously, provided all added tracer substances are synthesized with stably located labels (8).

Occasionally the situation may be such that the investigator desires to follow a very small amount of substance through a complicated system of some sort. In such a case, the material is synthesized with a radioactive atom and treated as if it were a normal compound. For purposes of analysis a known amount of inactive material, which may be very large compared with the amount of tracer material used, is added to the sample. Again, a portion of the pure mixed compound large enough for radioactivity analysis is isolated and its specific activity determined. In this instance the figure a is desired, the ratio Z is computed, b is known, and

$$a = \frac{b}{Z - 1}$$

A modification of this method has been applied to the microanalysis of mixtures, in the research cited, of protein hydrolyzates (10).

The mixture is treated with a labeled reagent, forming quantitatively a stable derivative of the desired component. A very large excess of unlabeled derivative is added to the mixture and a portion is purified to constant activity. If b milligrams of inactive material are added to the mixture containing a milligrams of labeled derivative, then a and b are related as in the equation above, where Z is the specific activity of the labeled derivative (computed from that of the reagent) divided by the specific activity of the purified mixed derivative. In most cases, Z is much greater than 1 and $a = b/Z$.

The method can be used with either radioactive or stable labels. In analyses of this type it is necessary that the sample be pure and completely free of labeled contaminants.

PURITY

In inorganic tracer applications questions of purity, as they affect the accuracy of analysis, are not usually of great importance because of the relative ease with which inorganic compounds can be separated. In the course of almost every investigation of organic or biological systems involving tracers it is necessary to isolate one or more compounds from a mixture of several. After a compound has been isolated it is necessary to establish rigorously the identity and especially the purity of the substance, and to show that the isotopic label that is measured belongs to the compound itself and not to a trace of some contaminant of relatively higher specific activity.

Organic chemists have used a number of criteria for purity and identity for many years. Melting points are valuable sources of evidence as to the identity of a compound, and considerable information concerning purity is obtainable from the sharpness of

the melting point. The density and refractive index are characteristic physical properties, most useful with liquids. Quantitative analysis for various elemental constituents gives considerable data on the nature of the substance and its gross purity. A number of other means are available for this purpose: specific rotation, absorption spectra, x-ray diffraction, solubility, etc. Any or all of these ordinarily sufficient criteria may be applied to an isotopic compound, and yet the results obtained from the determination of isotopic concentration may be in serious error. This is particularly true when substances of very high specific activity are employed, for a trace undetectable by the ordinary means of establishing purity may activate the gross sample to such an extent that incorrect conclusions would be drawn.

A number of procedures have been applied to this problem: crystallization, chromatography, distillation, distribution between solvents, etc. No one of these can assure success, but proper combination with other techniques can result in completely reliable data.

Isotope dilution techniques are especially susceptible to hazards of purity, and extraordinary precautions must be taken to eliminate the possibility of contamination, which, naturally, is particularly likely when the compounds found in a mixture have similar properties. Carrier technique is a valuable tool in dealing with small quantities of isotopically labeled compounds. If an inactive compound is added in sufficient quantity to be manipulated and purified, any activity appearing in the compound must have originated from labeled compound present in the mixture, provided the purified diluted sample is free from contamination; as the amount of inactive added carrier is known the amount of active compound in the mixture can be computed from the specific activity of the isolated sample. This particular variety of isotope dilution analysis is very susceptible to errors due to contamination. A somewhat less hazardous variation consists in the addition of labeled compound to an unlabeled mixture followed by reisolation and purification, and determination of the decrease in isotope concentration. In this process, the only isotope present is that introduced as part of the compound added, and the problem of contamination by small amounts of impurities of high specific activity is absent.

In order to analyze for a known compound in a complex mixture the following steps are suggested as a means of establishing its identity and purity (7):

1. A known quantity of carrier is added to the mixture.
2. By means of solvent extractions at various pH's, the compound—for example, if an acid—can be separated from neutral and basic materials.
3. Some preliminary method is used to effect a separation from other members of the same solubility class. Chromatography, distillation, and distribution are among the methods which are applicable.
4. The compound, if a solid, is recrystallized from different solvents to constant isotopic concentration. If it is a liquid, it should be converted into some solid derivative.
5. After this purification, the compound is converted to a derivative which is also recrystallized to constant isotopic concentration.
6. A comparison is made between the distribution coefficient determined from radioactivity measurements and that derived from conventional means. If they are identical, the compound is probably pure.
7. If desired, the compound is degraded to show the position of the label within the molecule. If identification of an unknown compound is desired, no carrier is added but steps 2 and 3 are carried out.
8. A number of chemical reactions are carried out by means of the distribution technique, and as many quantitative and qualitative data are collected as possible.
9. If the substance is present in such small quantity that ordinary physical methods, such as spectroscopy and polarography, are inapplicable and isolation is also impossible, it is often possible to make a guess as to the identity of the compound on the basis of the evidence already collected. The compound suspected can then be subjected to the same type of reactions to see whether there is close correspondence with the data obtained by isotopic measurement. If so, the compound may be

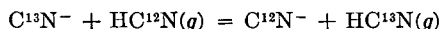
added as carrier, and the steps previously outlined are carried out. If the first compound does not carry the isotope, it may be possible to add others until success is achieved.

These procedures may seem long and tedious, but only a systematic study of this type can furnish information that can be interpreted with complete confidence.

ISOTOPE EFFECTS

Isotope effects are influences upon reactions due to the presence of a radioactive label or of an abnormal mixture of stable isotopes. The different weight atoms, of which the "normal" stable elements are composed, have slightly different properties due to these variations in atomic weight. The ordinary chemical properties of a given element are somewhat dependent upon the proportions in which the different stable isotopes are mixed. A change in this composition results in a change in properties.

Radioactive tracers are either lighter or heavier than the stable isotopes of a given element, and it is to be expected that this difference will exert a noticeable effect on the reactions of the element when the actual mass difference represents an appreciable fraction of the atomic weight. This effect is not a new difference in the behavior of the normal isotope mixture, but a departure from ordinary behavior because the tracer and normal atoms do not have identical properties. Thus the differences in behavior of tritium (H^3) and normal protium (H^1) are considerable. We would expect that all the physical and chemical properties of TCl , T_2O , T_2 , etc., would be very noticeably different from those of the corresponding protium compounds. Similarly, the properties of $C^{14}O_2$ and $C^{13}O_2$ should be slightly different from those of $C^{12}O_2$ under ordinary circumstances. The effect of the mass difference in general will not be the same for all chemical combinations of a given isotope, for it is known that the equilibrium constant of a reaction such as



is not unity. The constant for this reaction is actually 1.012 at $25^\circ C.$ and use can be made of this fact to concentrate the heavy isotope of carbon in hydrogen cyanide (9, 17, 20). Because of this small departure of the equilibrium constant from unity, isotopic exchange reactions have been used, in processes involving successive establishment of many equilibrium states, to concentrate C^{13} , N^{15} , etc.

The most important effect of isotopic labeling is to change slightly the rate of reaction in one direction and to exert less influence on the reverse reaction rate, as above. In reactions that do not approach an equilibrium state under the conditions employed, this difference in reaction rate of the two, or more, isotopic species present can, in some situations, be used to enhance isotope concentrations; but, more important, such effects bear heavily upon the interpretation of information obtained through the agency of isotopic tracers.

One might wish to measure the rate of diffusion of solid copper metal into silver sulfide at high temperature. It would probably be convenient to employ a radioactive tracer in this investigation, but one could not really say that the rate of diffusion of the tracer is the same as the rate of diffusion of the ordinary isotopes; indeed, even the stable isotopes might diffuse into the silver sulfide at different rates. Admittedly, such considerations become important only when very accurate information is desired, but the existence of such effects must be considered. The experiment described above has actually been performed (12). Stable copper is made up of two isotopes of mass number 63 and 65 whose relative abundances are 70.1 and 29.9, respectively. After 16 hours' contact at 450° , the isotopic constitution of the copper atoms diffused into silver sulfide is found to be mass number 63, 71.2 and mass number 65, 28.8. This enhancement is small, but the important thing is that it is so large with isotopes of such high atomic weight. When lighter tracers are employed, larger effects are noted.

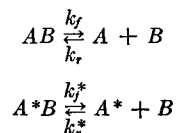
Admittedly, isotopic exchange reactions and solid-solid diffusion processes cannot be classified as ordinary chemistry. It has

been implied that appreciable isotope effects are to be found in a variety of simple chemical processes.

It is known that the dissociation probability of the $C^{12}-C^{12}$ bond is somewhat greater than that of the $C^{12}-C^{13}$ bond (and, by extension, greater than that of the $C^{12}-C^{14}$ linkage) (1). Suppose that phenylacetic acid were obtained as the end product of some study and it was desired to measure the concentration of heavy label (say C^{14}) in the carboxyl group, this carbon to be obtained by thermal decarboxylation of the acid. When half of the acid has been decomposed, less than half of the label is found in the effluent carbon dioxide; there is a competition among all the acid molecules present at any instant and, because of the difference in bond dissociation probabilities, $C^{12}O_2$ is evolved more rapidly than the labeled dioxide, the relative concentrations of their parent molecules being considered. If the reaction is driven to completion, all of the label is evolved and this enhancement of the activity of the residue disappears.

In order that this be true the initial condition must have been somewhere reversed and the heavy isotope would be evolved, for some period, proportionately more rapidly than the light one. This argument presupposes both a difference for the labeled and normal molecules in the specific rate constants for decarboxylation, and a unidirectional (nonequilibrium) process.

To illustrate, consider a general dissociation process involving a compound AB in the case where an amount of substance containing two isotopes of A is decomposed. The mixed reactions, with the corresponding specific rate constants indicated, are:



The equilibrium constants for these reactions are:

$$K = \frac{k_f}{k_r} = \frac{(A)(B)}{(AB)} \quad \text{and} \quad K^* = \frac{k_f^*}{k_r^*} = \frac{(A^*)(B)}{(A^*B)}$$

If the systems are combined so that simultaneous dissociation equilibria are established, then

$$\frac{K}{K^*} = \frac{k_f/k_r^*}{k_r/k_r^*} = \frac{(A)/(A^*)}{(AB)/(A^*B)}$$

A somewhat analogous formulation is derived when considering the isotopic exchange reactions, but the small departure from unity of K/K^* in such cases (with due regard for complications due to differences in symmetry number) does not imply that k_f/k_r^* or k_r/k_r^* shall not be greatly different from unity; large specific rate ratios have been observed for reactions involving the isotopes of hydrogen. The suggestion of the expression derived above is that equilibrium processes are unfavorable for simple observation of certain isotope effects.

If no reverse (association) reaction occurs, as in phenylacetic acid decarboxylation,

$$d(A) = k_f(AB)dt \quad \text{and} \quad d(A^*) = k_f^*(A^*B)dt$$

For the combined system,

$$\frac{d(A)}{d(A^*)} = \frac{k_f}{k_f^*} \times \frac{(AB)}{(A^*B)}$$

Making the substitutions:

$$(AB) = (AB)^o - (A) \quad \text{and} \quad (A^*B) = (A^*B)^o - (A^*)$$

where the superscript o indicates an initial value, and rearranging, it is found that

$$\frac{d(A)}{(AB)^o - (A)} = \frac{k}{k^*} \times \frac{d(A^*)}{(A^*B)^o - (A^*)}$$

Upon integration this becomes:

$$\ln \frac{(AB)^o - (A)}{(AB)^o} = \frac{k}{k^*} \ln \frac{(A^*B)^o - (A^*)}{(A^*B)^o}$$

or

$$\frac{\ln \frac{(AB)^o}{(A^*B)^o}}{\ln \frac{(A^*B)^o}{(A^*B)^o}} = \frac{k_f}{k_f^*}$$

If time is not canceled out, a different expression

$$\frac{(A)}{(A^*)} = \frac{(AB)^o}{(A^*B)^o} \frac{(1 - e^{-k_f t})}{(1 - e^{-k_f^* t})}$$

is obtained. From this formulation it can be seen that for small values of t , slight decomposition,

$$\frac{(A)}{(A^*)} = \frac{k_f}{k_f^*} \times \frac{(AB)^o}{(A^*B)^o}$$

which corresponds to the proportionately greatest enhancement of the effluent in $C^{12}O_2$ in the example above, while for large values of t , virtually complete decomposition,

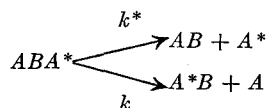
$$\frac{(A)}{(A^*)} = \frac{(AB)^o}{(A^*B)^o}$$

which corresponds to complete conversion of element and label to carbon dioxide and no net enhancement, no isotope effect.

It is seen that in a case ordinarily considered quite uncomplicated, appreciable isotope effects can be noted if complete reaction is not achieved.

Consider now the case where a symmetrical dicarboxylic acid, such as malonic acid, is decarboxylated to form a monoacid and carbon dioxide. Suppose that through synthesis, only one carboxyl group contains the heavy label—i.e., no molecules are doubly labeled. As the decarboxylation proceeds, the concentration of label atoms in the carbon dioxide is somewhat less than that in the original acid group, and that of the C^{14} in the carboxyl group of the acetic acid formed is somewhat greater; but the isotopic constitution of the label in the remaining diacid is unaffected by this process, because both functional groups on each molecule are capable of decarboxylation, but only one group can be decomposed. Thus, in the case of malonic acid it is actually found that this enhancement, which is predictable from considerations of the effect of the slightly heavier label atoms on the decarboxylation probability of a carboxyl group, is sufficiently large to result in rupture of $C^{12}-C^{12}$ and $C^{12}-C^{14}$ bonds in the ratio of 53/47 instead of 50/50, and that the label content of the acetic acid produced is some 12% greater than that of all the carbon dioxide evolved (21). This particular reaction is carried under rather mild conditions, malonic acid decarboxylates upon melting (135°C.), but similar enhancements of label concentration have been noted in the electron bombardment (1) and thermal cracking (500°C.) of propane (19).

The symmetrical functional group case lends itself easily to treatment if one makes the simplifying assumption that each functional grouping contains but one isotope—i.e., that all pairs of functional groups are completely heteronuclear with respect to carbon. [The actual situation, in which mixtures of isotopes are found in each group, has been studied by Bigeleisen (2)]. The schematic formulation for the unidirectional process is:

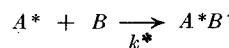
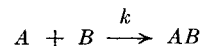


$$\frac{d(A^*)}{dt} = k^*(ABA^*), \quad \frac{d(A)}{dt} = k(ABA^*), \quad \text{and} \quad \frac{d(A)}{d(A^*)} = \frac{k}{k^*}$$

This corresponds to a constant enrichment of the effluent in the lighter isotope.

It is possible that certain biological processes can exhibit appreciable isotope effects in similar fashion. One can infer this from the measurements by Nier *et al.* (13, 14) of the ratio C^{12}/C^{13} in various materials. In general the ratio is higher for carbon derived from plants, coal, etc., than for carbon from the air, rocks, etc. This would seem to indicate that living plants are able to accept, during photosynthesis, $C^{12}O_2$ at a somewhat greater proportionate rate than $C^{13}O_2$.

If A represents $C^{12}O_2$, A^* $C^{13}O_2$, and B the carbon dioxide acceptor in the plant,



Then,

$$\frac{-d(A)}{dt} = k(A), \quad \frac{-d(A^*)}{dt} = k^*(A^*), \quad \text{and} \quad \frac{-d(A)}{d(A^*)} = \frac{k}{k^*} \left[-\frac{d(A^*)}{d(A^*)} \right]$$

This expression can be integrated to give

$$\frac{\ln \frac{(A)^o}{(A)}}{\ln \frac{(A^*)^o}{(A^*)}} = \frac{k}{k^*}$$

where o represents an initial concentration.

This effect, impoverishment of the atmosphere in the lighter isotope, has been observed, semiquantitatively, during the photosynthetic uptake of $CO_2-C^{14}O_2$ mixtures by barley leaves (4). The effect is so pronounced that the specific activity of the atmospheric radiocarbon dioxide reaches, at one point, a figure some 1.2 times its original value under the conditions of the experiment.

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Radiochemical Activity Analysis

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Radiochemical activity analysis is defined as the identification and determination of the radioactivity due to individual constituents in mixtures of radioactive materials. Physical methods of identification of individual radioactivities and chemical methods for the resolution of mixtures are described. Addition of a known amount of inactive carrier and determination of the efficiency of recovery of the isolation process permit short-cut methods to be used in quantitative determinations and greatly cut the time necessary for an analysis. Methods for the rapid determination of radioactivity due to each of the fission elements have been developed and the procedure for zirconium activity is discussed in detail. Applications in radioactive tracer production and utilization are suggested.

RADIOCHEMICAL activity analysis involves the identification or determination of the elements or compounds responsible for the radioactivity of mixtures. As with other types of chemical analysis, activity analysis may be qualitative if it is desired merely to identify the elements or compounds responsible for the radioactivity, or it may be quantitative if the fraction of the total radioactivity due to a given constituent is to be determined. Activity analysis should be carefully distinguished from ordinary chemical analysis, for frequently the results of the two bear no relationship to each other. A typical rare earth tracer preparation if submitted for chemical analysis might be found to contain nothing but dilute hydrochloric acid, a trace of silica, and miscellaneous microimpurities. Subjected to radiochemical β -activity analysis, the same sample might be reported as 58% yttrium, 40% cerium, and 2% lanthanum.

Activity analysis is important for the identification of artificially produced radioactivities and the determination of the composition of mixtures of artificial and natural radioactivities. Analysis may be made for α -, β -, or γ -activities; the general principles involved are the same in each case except for the actual physical measurement of the radioactivity.

QUALITATIVE ACTIVITY ANALYSIS

If a single radioisotope is believed to be present in essentially pure form, it is often possible to identify it by purely physical methods. Each radioisotope has its own individual radiation and decay characteristics, and these may be measured with the relatively simple apparatus used in ordinary radiochemical tracer work. With α -emitters, a measure of the α -ray energy may be obtained either by determination of the range of the α -particles in air or by electronic measurement of the pulse height in the conventional α -chamber (1).

The energy characteristics of β -emitting isotopes, which are the ones most commonly used, may easily be determined by measuring the aluminum absorption curve of the radiation. By plotting the logarithm of the counting rate of a β -emitting sample against the thickness of aluminum (expressed in milligrams per square centimeter), introduced between the sample and the Geiger counter, characteristic curves are obtained for the various radioisotopes (Figure 1). If external conditions have limited the number of possibilities, it is often as easy to identify the isotope from the appearance of the absorption curves as to identify a compound as one of several by comparison of their ultraviolet absorption spectra. Numerical values for the maximum β -energy may be derived from these absorption curves by the simple and ingenious method introduced by Feather (4, 5).

Gamma-emitters do not give absorption curves as characteristic as those obtained with β -emitters, but measurement of the absorption half-thickness in lead provides a means of approximately estimating γ -energies.

Another useful characteristic of a radioisotope which may be applied to identification is the characteristic rate of decay usually expressed as the half-life. If the logarithm of the counting rate of a sample of a pure radioisotope is plotted against time, a straight line is normally obtained and the time necessary for the sample to decay to one half its original value may be estimated. A useful table of radioisotopes arranged according to half-lives has been compiled by Clark and Jones (2).

The component of a mixture of two or even three radioisotopes can be identified by purely physical means only if the radiations or half-lives differ sufficiently. The problem is analogous to the determination of the composition of binary and ternary mixtures by measurement of physical properties such as light absorption and index of refraction. If the mixture contains two radioisotopes with distinctly different maximum β -energies, the aluminum absorption curve will reveal itself as a composite of the two. If

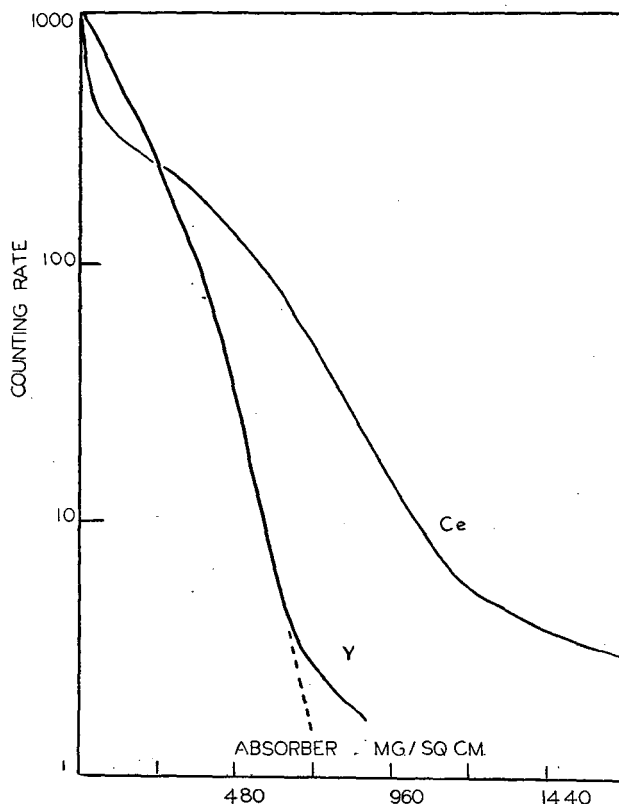


Figure 1. Aluminum Absorption Curves for Typical Fission Product Radioactivities

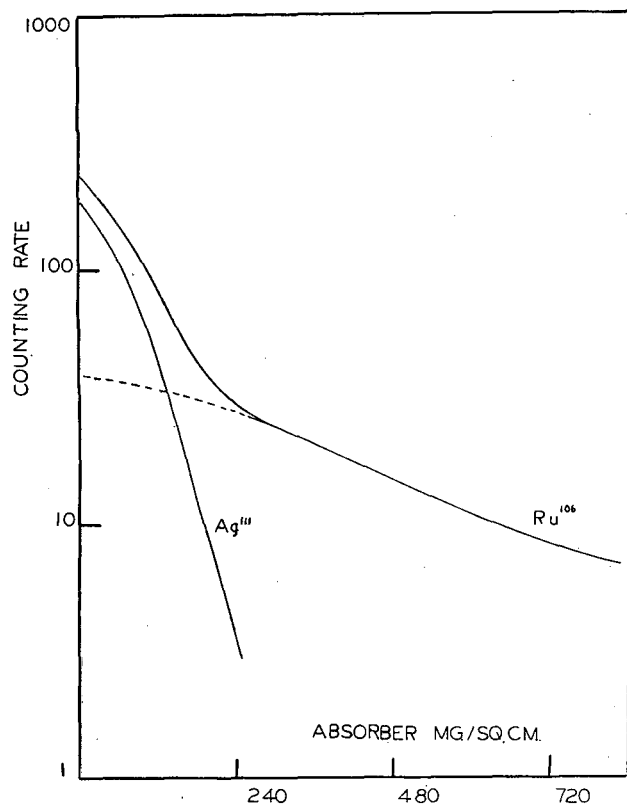


Figure 2. Composite Aluminum Absorption Curve

Mixture of Ag^{111} (1.0 m.e.v.) and Ru^{106} (3.1 m.e.v. effective β -energy), showing resolution into individual components

it is possible to estimate the contribution of the stronger β -emitter by extrapolation and subtract it from the total, the difference gives the contribution of the weaker constituent (Figure 2). Similarly, if two or even more constituents are present with clearly differing half-lives, it may be possible to resolve the mixture by allowing the short-lived components to decay away, leaving only the longest lived isotope, the half-life of which is easily determined. The contribution due to this isotope may be calculated for various times and subtracted from the total, leaving the contributions of the others. The next longest lived may be identified in the same way and subtracted in turn to give the next component. An example is shown in Figure 3.

Special cases exist where not only qualitative identification but quantitative analysis of simple mixtures is possible if the composition is known to be limited to two or at the most three familiar constituents. An example of the application of β -absorption measurements to this problem is the determination of cerium activity in yttrium tracer preparations made from uranium fission, which may be done very easily by placing enough absorber between the sample and the counter to cut out yttrium radiations. Any count observed would then be due to cerium impurity (Figure 1). From the relative counting rates of a pure cerium sample without absorber and with absorber sufficient to stop the yttrium β -rays, the contribution of the cerium to the total counting rate of the yttrium sample of zero absorber can be calculated. If a sample is fairly complex, or if the radiation characteristics are insufficiently different to permit this sort of simple physical analysis, chemical separation of the different radioactive elements or compounds is necessary.

QUANTITATIVE ACTIVITY ANALYSIS

The general procedure for the quantitative radiochemical analysis of a complex mixture involves: (1) sampling, (2) addition

of inactive carrier for the element or compound in question, (3) chemical separation and purification, (4) isolation of the desired constituent in a form suitable for counting and for the determination of the percentage recovery (chemical yield), (5) counting, and (6) calculation of the results. It is worth while to consider the significant features of each step in some detail.

Sampling. As in other forms of chemical analysis, the method of taking the sample is of great importance and the obtaining of a representative sample is often the most difficult step in the entire analysis, particularly if the radioelement sought is given to forming colloidal suspensions. The so-called "carrier-free tracers" may contain the radioelement in concentrations of the order of 10^{-12} molar, and such small amounts of material may easily be lost by adsorption on the walls of the container, traces of silica, and dust. Barium tracer in dilute hydrochloric acid, for example, is stable, but the same tracer in dilute sulfuric acid—even though the solubility product of barium sulfate is not exceeded—may yield very uncertain results due to adsorption of the barium on the walls of the sample tube and inside of the pipet. For each analytical method and type of sample the validity of the sampling procedure must be verified experimentally.

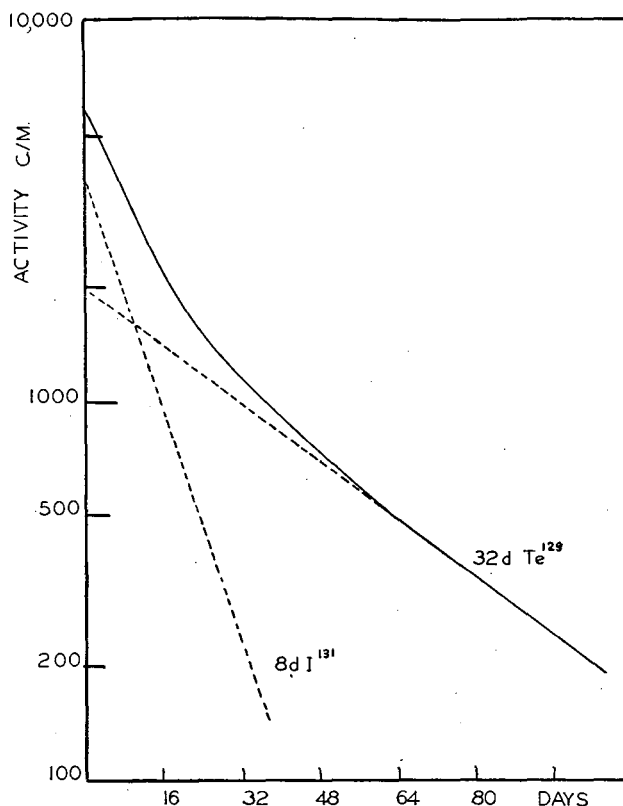


Figure 3. Composite Decay Curve

Mixture of $8d \text{I}^{131}$ and $32d \text{Te}^{129}$, showing resolution into individual components

Carrier. A known amount of the ordinary inactive isotope or isotopes of the element to be determined is added to serve as a "carrier" for the radioactive atoms and to give them the properties characteristic of the element in ordinary amounts, rather than the often unusual properties associated with extremely low concentrations. In general, one does not strive for a quantitative recovery of the carrier but is content with recovering a substantial portion of it in a pure state and correcting his result for the amount lost. This has the obvious advantage of permitting rapid work without taking pains to make recovery quanti-

tative. Any separation may be used which yields a pure product, even though the recovery may be far from complete. This is an important advantage if speed is essential, especially with the more difficult elements such as columbium, zirconium, and the rare earths. It is possible, for example, to determine columbium activity quantitatively in the presence of zirconium and the rare earths in about one hour. Obviously, if the original sample already contains significant amounts of the element or substance to be determined, the ordinary carrier method cannot be used. The constituent in question must be isolated quantitatively in the activity analysis or the total amount determined before the separation process is begun.

The carrier method is based on the assumption that tracer and carrier always have exactly the same properties. This is generally true, but certain exceptions must be noted. If carrier and tracer are in different chemical states—e.g., iodide and iodate in alkaline solutions—and these do not interact with each other (exchange), subsequent chemical treatment may separate the active and inactive atoms and give an entirely erroneous result. It is therefore necessary to ensure that active and inactive atoms all reach the same chemical state before any separation step is applied.

An example of exchange difficulty can be found in the determination of tellurium activity. If the radioactive tellurium is present as tellurate and the carrier is added as tellurite, the rate of exchange between the two is ordinarily slow. Precipitation of the tellurite as metallic tellurium by reduction with sulfur dioxide in hydrochloric acid removes it quantitatively, but most of the tellurate tracer is unaffected and remains in solution. Hence, the first step in activity analysis is frequently a rather drastic one chosen to convert tracer and carrier to the same chemical state.

For certain elements such as technetium, plutonium, and promethium, no inactive isotopes exist for use as carriers. Recourse must then be made either to the use of a nonisotopic but chemically very similar carrier—for example, another rare earth in the determination of promethium—or to rigid quantitative isolation of the radioelement directly. The latter is ordinarily difficult, but possible if suitable precautions are taken.

Chemical Separations. Subsequent chemical separations are designed with two objectives in mind: radiochemical purity of the tracer and chemical purity of the carrier. One must be certain that all interfering radioactivities are removed during these operations and it must be remembered that if the impurities are present in very low chemical concentrations, their chemical behavior may be different from that observed when they are present in macroamounts. This difference may be either to the advantage or disadvantage of the analyst. Experiment determines the number of individual steps necessary to give adequate decontamination. Evidently the determination of small amounts of active impurities in a relatively pure tracer preparation requires better decontamination than the determination of the major constituent. The achievement of satisfactory chemical purity in the recovery of the carrier is usually not difficult.

Isolation of Carrier and Determination of Chemical Yield. When satisfactory chemical and radiochemical purity has been achieved, it is necessary to determine the radioactivity of the final product and the completeness of recovery. A saving in time is possible if the radioactivity and chemical measurements can both be done with the sample in the same physical state. Radioactivity is usually determined in solid samples and for this reason the chemical yield is most often determined gravimetrically by weighing the final sample just before or after counting it. With the development of satisfactory liquid counters it is likely that more frequent use will be made of colorimetric and volumetric methods for the determination of chemical yields. For most samples which are counted as solids, determination of the chemical yield with an accuracy of $\pm 2\%$ is sufficient, as the radioactive measurement is not so good as that. If the yield is to be determined gravimetrically, the mounted

sample must be pure and of known composition. If volumetric or colorimetric determination of the chemical yield is used, only those elements which would constitute interferences need be removed.

Counting. Surprisingly enough, the measurement of the radioactivity of the isolated sample is frequently the most inaccurate and unsatisfactory step in the entire analysis. This is particularly true if the radioisotope is a β -emitter and is counted by placing the solid sample near a Geiger tube—the most common method of counting. Information is widely available on the magnitude of the error produced through statistical fluctuations in radioactive decay (8), and tables and graphs have been prepared showing how long it is necessary to count to get 10, 1, or 0.1% precision. The ordinary errors inherent in the use of Geiger tubes are also well known—namely, the effect of coincidence losses at high counting rates, and the unpredictable fluctuations in counter efficiency which are also observed (8). Unfortunately, many workers have not realized that these effects are virtually negligible in comparison with the differences that may arise in β -counting rates through small differences in the physical form of the mounted sample. Several important factors enter into the apparent counting rate of a solid sample of the sort a chemist is usually interested in, mounted in the conventional way under an end-window Geiger tube. These include geometry factor, absorption due to air, window, cover, and the sample itself, and the efficiency with which the material on which the sample is placed reflects (scatters) downward-directed β -particles back upward into the counter. Beyond these is one other very important factor: the efficiency with which the sample itself scatters its own radiations. This phenomenon, known as self-scattering, is the major obstacle to accuracy with this type of counting.

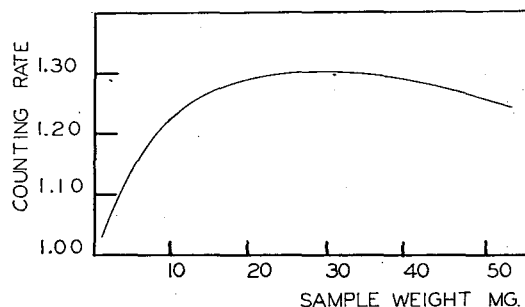


Figure 4. Typical Self-Scattering Curve for β -Emitter of About 1.5 M.E.V. Energy
Mountings on watch glasses in standard counting arrangement

EFFECT OF PHYSICAL FORM OF SAMPLE. The effect of the physical form of the mounted sample on the counting rate has been described in an important paper by Engelkemeir, Seiler, Steinberg, and Winsberg, which has for several years been awaiting publication as part of the Plutonium Project Record (9). The problem was studied independently by Hume, Sadowski, and Mahlman (7) at the same time as the other workers, and the report of these results is likewise awaiting appearance of the National Nuclear Energy Series. The essential features of these studies are summarized below.

If identical small portions of an essentially carrier-free tracer solution are evaporated in the same small area in the centers of a series of uniform metal plates or in small metal cups and these samples are counted, good results are obtained. But if to each of these samples is added during evaporation a significant amount (5 to 50 mg.) of solid material, the counting rates of the different samples no longer agree. If a plot is made of the observed counting rate of the fixed amount of tracer evaporated with varying amounts of carrier against the amount of carrier used, a curve which frequently has the form shown in Figure 4 is obtained.

The counting rate increases with increasing carrier, passes through a maximum, and then decreases, owing to self-absorption. The increase over the zero carrier count may be as high as 30%. Individual points on the curve reproduce poorly; 10% differences are not uncommon, although the order of magnitude of the effect is never in doubt. A curve obtained not by evaporation but by precipitation of increasing amounts of carrier with the tracer and filtering and mounting the precipitates will have somewhat better reproducibility. The scattering effect is dependent upon the physical form and particularly upon the density of the solid substance as well as the energy spectrum of the radioisotope. The counting of solid samples is therefore highly uncertain unless all in a series have exactly the same physical form and the total weight is always about the same. It is not possible to compare a sample evaporated on a plate with another in the form of a precipitate transferred to a similar plate.

The author has observed repeatedly, for example, that a pure yttrium tracer evaporated to dryness on a watch glass with 20 mg. of yttrium carrier as the nitrate gave results as much as 20% below those obtained when the activity was precipitated as the oxalate with the same amount of yttrium carrier, filtered, and transferred to a watch glass for counting. A similar experience was encountered with a sample of ruthenium tracer. Samples of the tracer were evaporated with added ruthenium chloride as carrier in porcelain counting dishes of the sort frequently used in biological work. After counting, the samples—still in the same dishes—were ignited in hydrogen to reduce the carrier ruthenium to the metallic state. On remeasurement, the counting rates were found to be approximately 10% higher.

An examination of the literature reveals that successful tracer applications have always involved a rigid standardization of counting conditions. For the research worker using a single isotope and able, in general, to set his counting conditions as he wishes, this does not involve any great difficulty. For the analyst who must try to make sense out of results obtained on a sample "as received," the lack of a universally applicable method of preparing samples for comparative counting is a major obstacle.

The direct counting of β -activity in solutions has received comparatively little attention in the past, but the obvious advantages involved make the method appear attractive in spite of difficulties due to self-absorption and contamination of the counting apparatus. It is not unlikely that liquid counting may ultimately surpass solid counting in popularity for radioisotopes that emit moderately strong β -rays. The measurement of α -activity involves difficulties also, but these are primarily due to absorption and are well understood. Comparatively little work is done with α -emitting isotopes in comparison to that which is done with β - and γ -emitters and therefore no extensive discussion is given here.

The measurement of γ -activity is in some respects much simpler than the measurement of β -activity, since γ -rays do not scatter and the physical state of the sample is of relatively little consequence. Good precision can be obtained in the measurement of γ -radiation by several different methods—Geiger tubes, electroscopes, high pressure ionization chambers, and scintillation photomultipliers; to mention only four. The difficulty lies in the fact that the observed result is always dependent upon the nature of the apparatus used and it is extremely difficult, without direct experimental comparison, to correlate the results obtained by one method with those obtained by any of the others. Further than that, comparatively minor variations in the apparatus produce considerable differences with any one of the methods of measurement.

In most laboratories γ -activity is measured with an ordinary Geiger tube by inserting between the sample and the tube an absorber sufficiently thick to stop all β -particles. The γ -rays themselves do not produce counts but instead eject Compton and photoelectrons from the absorber or the tube itself and these particles are what is detected by the Geiger tube. The counting

efficiency depends on the tube, the nature of the absorber used, and the energy of the γ -ray.

On the Manhattan Project, there were at least three absorbers in common use for γ -counting: a slab of aluminum of thickness equivalent to 1.7 grams per sq. cm., a sheet of lead with a thickness equivalent to 1.9 grams per sq. cm., and a "sandwich" consisting of a 1.9 gram per sq. cm. sheet of lead with 1.7 grams per sq. cm. of aluminum underneath and a sheet of about 130 mg. per sq. cm. of aluminum on top. The sandwich, which is the invention of W. H. Sullivan, is based on the following principles:

The thick aluminum takes out the β -particles but with the production of soft x-rays (*Bremsstrahlen*), the lead serves to filter out the x-rays, and the top aluminum sheet eliminates photoelectrons emitted from the lead. This leaves, theoretically, only Compton electrons from the top aluminum sheet to be counted and the counting rate should be proportional to the intensity of the γ -rays. The counting rate with such an arrangement should have a closer correlation with the actual γ -disintegration rate than the counting rate obtained with the simpler absorbers.

The results obtained by counting the same samples with the different absorbers vary greatly. The magnitude of the variation is dependent upon the energy of both the γ -ray and the β -rays being absorbed. Typical results are given in Table I, where the counting rates of samples of three tracers are compared under each of the three standard counting conditions. An analyst who found 1.0% γ -activity due to cerium by the sandwich method would not agree with another analyst who used aluminum alone, for the latter would report 5.4%! There is a real need for widespread standardization of γ -counting conventions and inter-comparison of various γ -counting methods.

Table I. Comparison of Relative γ -Counting Rates with Different β -Ray Absorbers

Radioisotope	Sandwich	Pb. 1.9 G./Sq. Cm.	Al, 1.7 G./Sq. Cm.
Ce ¹⁴¹	(1.00)	2.07	1.49
Ce ¹⁴¹ - ⁴	(1.00)	4.07	5.42
La ¹⁴⁴	(1.00)	1.63	1.49

For each isotope counting rates are reported in terms of ratio of observed rate to rate obtained with sandwich.

Calculations. If a sample is counted in the usual manner, the observed counting rate is corrected for background and normalized to standard counter efficiency. A correction may also be applied for self-absorption of the sample. If the radioisotope is short-lived or undergoes rapid daughter growth, the observed counting rate may need to be corrected to some standard comparison time by the usual equations of radioactive decay. The final count is then corrected for losses during the chemical operations.

A concrete illustration might be the determination of P³² β -activity in a mixture of carrier-free phosphorus, cobalt, and cesium tracers which had a total radioactivity of 4000 counts per minute per ml. at 8:00 A.M. Thursday. To 5.00 ml. of solution was added phosphorus carrier equivalent to 54.0 mg. of magnesium ammonium phosphate hexahydrate. After appropriate chemical steps, 42.7 mg. of magnesium ammonium phosphate were recovered, chemically and radiochemically pure. At noon on Friday this sample counted under standard conditions 5000 counts per minute. Corrected for the chemical yield of 79%, the count was 6330 counts per minute of phosphorus in the 5-ml. sample. Referred back to 8:00 A.M. the previous day by allowing for decay of the 14.3d P³² the count would have been 6700 counts per minute, or 1340 counts per minute per ml.: in other words, 33.5% of the total. At other times, because the several isotopes in the mixture decay with differing rates, the percentage composition would not be the same.

APPLICATIONS

During the war, the research and development program of the Plutonium Project required an unprecedented number and vari-

ety of radiochemical activity analyses for the fission products of uranium. The bulk of the research papers by a large number of workers, principally under C. D. Coryell, N. Sugarman, and D. N. Hume, is scheduled for publication in Volume 9B of the Plutonium Project Record. A brief review of the methodology and a few examples are given here, as the work provides a particularly apt illustration of the general principles involved.

Table II. Flowsheet of Radiochemical Activity Analysis for Zirconium

Sample. Ppt. LaF ₃ plus rare earths Ba Sr UX activities (Discard)	Add HNO ₃ , Zr carrier, and HF. Add La carrier	
	Soln. U, fission products (Discard)	Soln. U, Zr, fission products. Add Ba carrier
		Ppt. BaZrFe. Dissolve in HNO ₃ and H ₂ BO ₃ . Reprecipitate. Redissolve and add H ₂ SO ₄
		Ppt. BaSO ₄ (Discard) Soln. ZrO ⁺⁺ with cupferron, ignite to ZrO ₂ , and weigh. Measure radioactivity

Procedures were developed for the rapid determination of the activity due to each of the fission elements, other than the noble gases and certain rare earths, in the very complex mixtures of activities resulting from uranium fission. The general procedure for each element was as outlined above.

Procedures were developed in which liquid samples up to 5 or 10 ml. were used and most operations were conducted in 50-ml. centrifuge tubes. Centrifugation rather than filtration was the preferred method of separation and in many respects the technique was similar to that of modern qualitative semimicroanalysis. Samples were chosen such that in general no health hazard due to radiation was encountered. Samples were invariably mounted on 2.5-cm. (1 inch) watch glasses for counting. Liquids were evaporated on the watch glasses together with enough solid material (usually cerous nitrate) to get a total weight of about 30 mg. to provide optimum self-scattering. At the conclusion of the analysis, the purified constituent was precipitated preferably in a form which could be filtered out on a previously weighed 2.2-cm. (0.875-inch) filter paper in a Hirsch funnel, dried with alcohol and ether or in an oven at 110° C., and weighed. The weighed precipitate together with its filter paper was then transferred to a watch glass for counting. Precipitates that required ignition were ignited in crucibles, weighed by difference onto watch glasses, and spread smoothly. The watch glasses were mounted on stiff 2.5 × 3.25 inch cards designed to fit the standard counting apparatus.

A typical example of activity analysis as applied to fission product mixtures is the determination of zirconium activity described below (6). The outline of the final chemical procedure is shown in Table II.

The sample of mixed fission product radioactivities is measured out into a 50 ml. Lusteroid centrifuge tube, and zirconium carrier and an excess of nitric and hydrofluoric acids are added. This serves to dissolve the zirconium as the very stable fluoride complex. It had been found that direct precipitation of zirconium as zirconium phosphate at this point resulted in the loss of much of the zirconium activity. Addition of oxalic acid to convert both tracer and carrier zirconium to the same form (oxalate complex) did not entirely correct the difficulty, but treatment with hydrofluoric acid served to ensure complete exchange between carrier and tracer. This was checked by comparative analyses and by experiments with pure tracers.

The first separation step involves the removal of rare earths together with much of the alkaline earths and uranium-X, if present. Lanthanum nitrate is added as a carrier for these elements. Upon the formation of a precipitate of lanthanum fluoride, rare earth and uranium-X radioactivities are carried down as insoluble fluorides. Barium and strontium, although soluble when present in macroamounts, are strongly coprecipitated by lanthanum fluoride when they are present in low concentrations, and they are removed also. The rare earth precipitate is centrifuged out, the solution is decanted into another tube, and the original tube together with its precipitate is thrown away. A second or third scavenging by addition of more lan-

thanum carrier may be desirable if the ratio of zirconium activity to rare earth and alkaline earth activities is low.

The next step involves the precipitation of the zirconium as barium fluozirconate for the separation from the other fission elements, especially columbium. Methods available in the literature for the separation of zirconium and columbium were found insufficiently complete or unsatisfactorily time-consuming. The separation by precipitation as barium fluozirconate offers as usually good separation of columbium from zirconium. Although the precipitate is fairly soluble, the yield is adequate, and the radiochemical purity is very high. Tracer experiments showed three precipitations to decrease the columbium activity contamination by a factor of 10⁶ and the removal of the other fission products was even better. The barium fluozirconate precipitate is nicely crystalline, comes down readily and rapidly, and is very easily dissolved afterwards in a mixture of boric and nitric acids. The boric acid serves to remove fluoride from solution as the stable fluoborate ion and is a very convenient means of aiding the solution of insoluble fluorides in general.

By this time the zirconium is essentially pure radiochemically. Before it can be precipitated as the cupferride for filtering and ignition to the oxide, the relatively high concentration of inactive barium present must be removed by precipitation with sulfate. Unless this is done, barium contaminates the final oxide sample and gives a result for the chemical yield which is several per cent too high. After the zirconium oxide has been weighed, it is transferred to a watch glass and the β- or γ-activity is counted in the usual way.

This procedure was tested by analysis of pure zirconium-free tracer preparations of all the common fission elements to demonstrate that those radioactivities did not come through the procedure. It was also tested by analyzing unseparated fission product mixtures and demonstrating that no significant radioactive impurities were present in the final zirconium precipitate.

The procedure described can easily be done in duplicate in less than 2 hours, and similar speed was found attainable with most of the other fission elements. The major sources of error were in sampling and counting. Results good to ±5% were usually satisfactory for the purposes in hand and only in unusual circumstances was an effort made to obtain accuracy higher than 2 to 3%. It is anticipated that as more radioactive tracers from pile and accelerator sources are marketed, many more standard methods of activity analysis will be developed and put into use. The existence of a reliable activity analysis procedure for a given element makes it possible to do tracer experiments with that element without first isolating the pure radioactivity. An unseparated mixture of carrier-free activities may be employed in the experiment and the samples analyzed for the particular element or elements of interest. This may be of considerable importance where tracer preparation is long and difficult, as the analysis procedure is usually comparatively short and simple.

ACKNOWLEDGMENTS

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Determination of Naturally Occurring Radioactive Elements

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Chemical and radiochemical methods are given for the determination of uranium and thorium. The chemical determination of uranium in ores is the more accurate method. Thorium in minerals is most accurately determined by chemical means but may be estimated radiochemically.

OF THE various radioactive elements occurring in nature, the series in which uranium is the parent member is the best known. The thorium and actinouranium series are less widely known. Interest has been shown only recently in the radioactivity of other naturally occurring elements such as potassium, rubidium, samarium, and lutecium.

Less than 20 years ago uranium was of interest chiefly as the "mother" of the uranium series and in its connection with radium. The roles are now reversed and radium has become of secondary importance. The interest in thorium has also changed. While years ago the interest in monazite was for the thorium content, it has recently shifted to the rare earths. Because thorium is a

fissionable element, however, this trend will no doubt be reversed and, in fact, will probably encourage a search for new sources for thorium.

The Atomic Energy Commission recently announced a program in which it guarantees a 10-year minimum price for domestic refined uranium ores as well as a \$10,000 bonus for the discovery and production of high grade uranium material. This program, in connection with the fact that by-products that contain as little as 0.05% uranium or thorium are considered possible source material and therefore have to be accounted for, has increased interest in the methods of analysis for these elements.

There is a possibility of using the radioactive properties of lute-

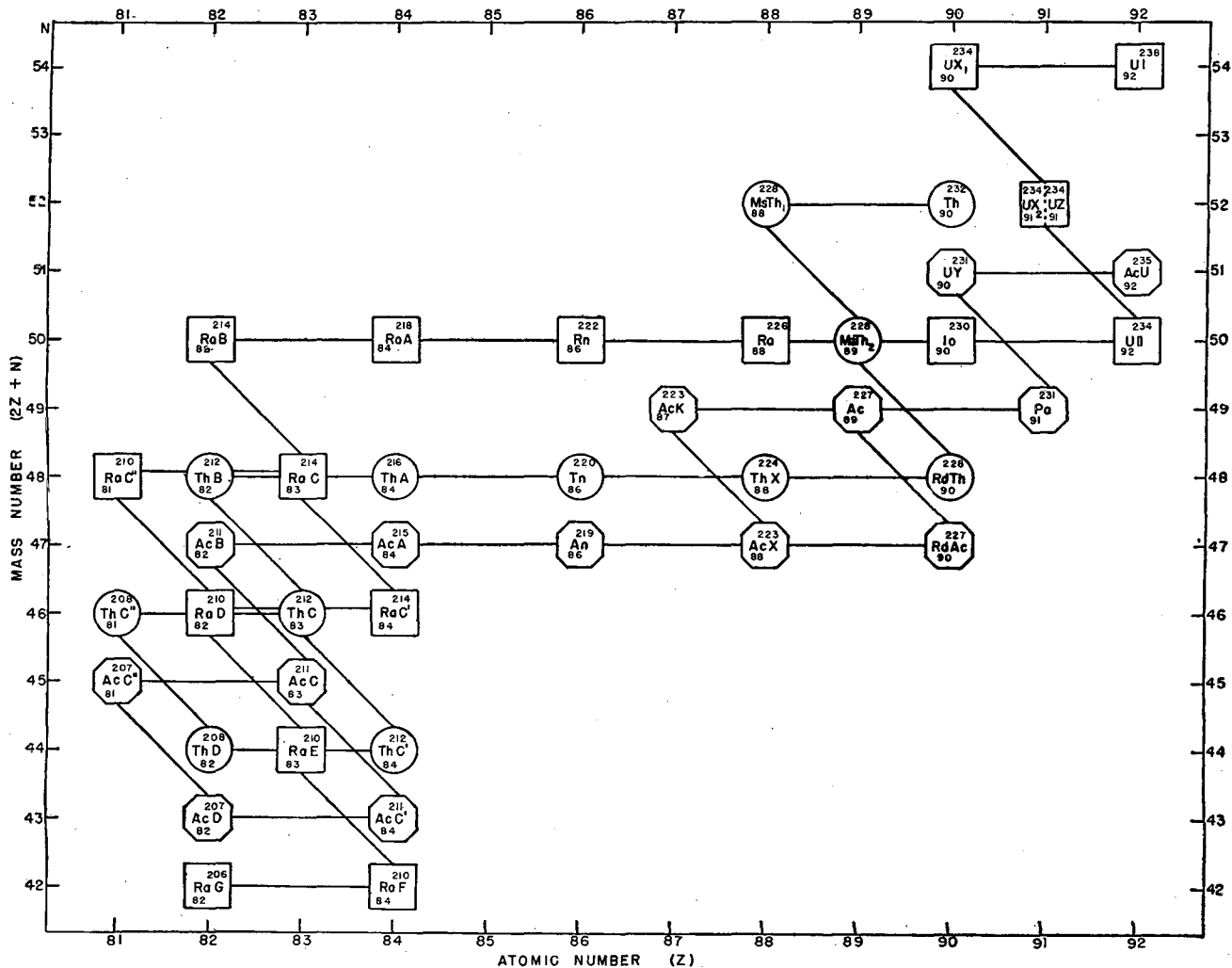


Figure 1. Uranium and Thorium Series Elements

cium and potassium (β) to determine these elements, but the following discussions treat of uranium and thorium, with reference to the other members of the series only in so far as they are used for determining these two elements.

THE URANIUM SERIES

The uranium series is shown in Figure 1.

The most important member is uranium ${}_{92}\text{U}^{238}$, with ${}_{88}\text{Ra}^{226}$, ${}_{86}\text{Rn}^{222}$, ${}_{90}\text{UX}_1^{234}$, and ${}_{82}\text{RaD}^{210}$ following in about that order. In all chemical work the other isotopes of uranium, ${}_{90}\text{AcU}^{235}$ and ${}_{92}\text{U}_2^{234}$, are considered.

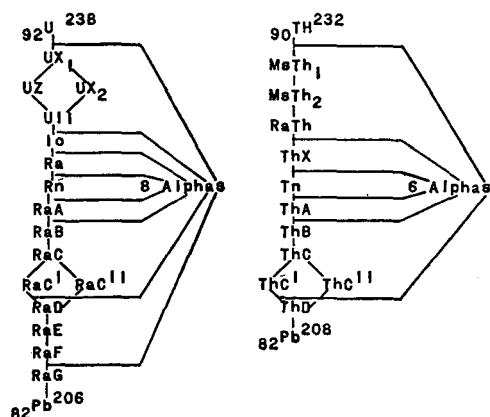


Figure 2. Alpha-Activity of Uranium and Thorium Series

In the determination of the most important element in this series, uranium, chemical methods are more reliable than radiochemical ones. The determination of uranium by means of radioactivity can be divided into methods employing α -, β -, or γ -radiation. The α -, β -, and γ -activity from the uranium and thorium series is shown in Figures 2, 3, and 4 (4). If uranium is in radioactive equilibrium, the amount of uranium present may be calculated by the determination of any one of the disintegration products.

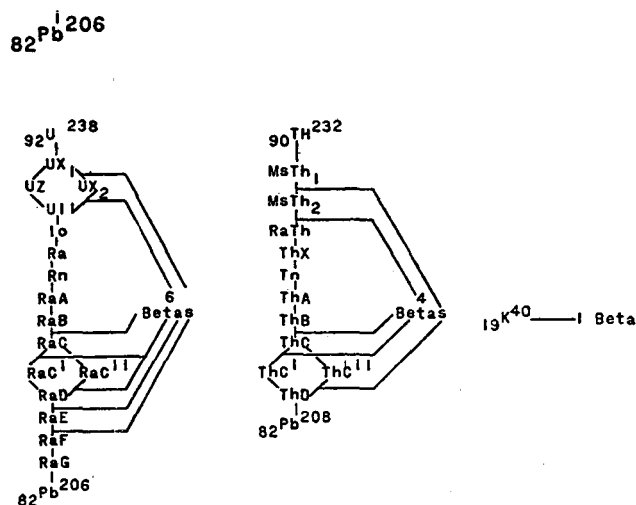


Figure 3. Beta-Activity of Uranium and Thorium Series

α -Ray Methods. INDIRECT METHOD. This method, which depends on equilibrium between uranium and its radioactive disintegration products and the absence of thorium, has been used for many years and is still used to some extent by prospectors. The material in which radioactivity is to be measured is intro-

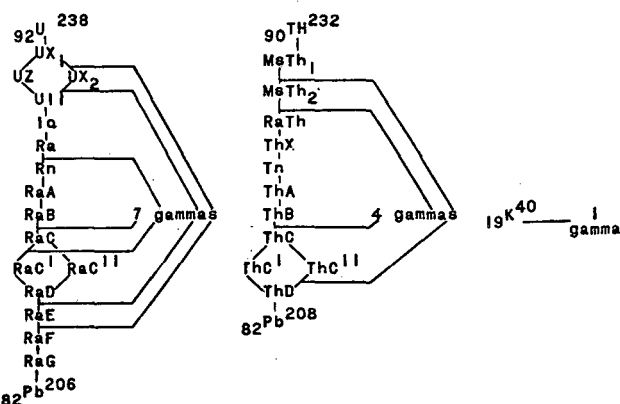


Figure 4. Gamma-Activity of Uranium and Thorium Series

duced into a charged electroscope chamber or into an ionization chamber, and the rate of fall of the charged leaf or the count is compared with samples that have been analyzed by chemical means (49). The results are erroneous if thorium is present, even though the sample is in radioactive equilibrium.

In certain cases, such as the α -helium method for determining geological ages (17), the α -particle emission is the chief interest. In this method the finely ground rock (30 to 70 mg.) is deposited in suspension on a weighed aluminum disk (44 sq. cm.) and the α -particles are then counted in a nitrogen-filled ionization chamber.

DIRECT METHOD. The determination of the α -activity after separating uranium and its isotopes has been used for determination of small amounts of uranium (79) and also for determination of the U^{235} - U^{238} ratio (40). While Urry used coprecipitation with iron and aluminum as a method for isolating the uranium, using an ether extraction of uranyl nitrate would no doubt be simpler.

DETERMINATION OF RADIUM. If equilibrium is assured, the uranium content can be obtained. The emanation method (49) is one of the most accurate ways of determining radium in ores and rocks. The first decay product of radium happens to be a gas, radon, which is a member of the inert series of gases. Although the quantity of gas associated with radium is minute, it can be collected and handled conveniently like any other gas.

The direct-fusion technique of measuring the radium content of rocks, described in detail by Evans (15), consists of fusing the material and boiling off the emanation at 2000°C . The radon is collected in double ionization chambers (shown in Figure 5) coupled to a string electrometer of high sensitivity.

In the other fusion method which has been used to a considerable extent, the material is fused in potassium bisulfate in a Pyrex tube for about 5 minutes and then allowed to cool. The time of solidification is noted, the tubes closed, and after a measured period of time the sample is refused and the gases are collected in an ion chamber. This method has not been found as applicable as that in which the sample is fused and completely dissolved in acid before de-emanation. The ability of radon to be adsorbed on glass is very marked (50) and must be considered at all times.

The method that has been used to a great extent for the determination of radium in ores and residues is as follows:

The sample of an ore is dissolved in nitric acid, the solution is filtered, and the residue is treated with hydrofluoric acid followed by a sodium carbonate fusion. This melt is dissolved in nitric acid, which is added to the original nitric acid leach. If a radium-bearing sludge is to be examined, the silica is removed with hydrofluoric acid and the residue is fused with sodium carbonate. This melt is then dissolved in nitric acid (78). In all cases a clear solution free from suspended silica is necessary because of the marked absorption of radon by silica.

The nitric acid solution is then placed in flask *S* (Figure 6) (12) fitted with a reflux condenser, and de-emanated by boiling at

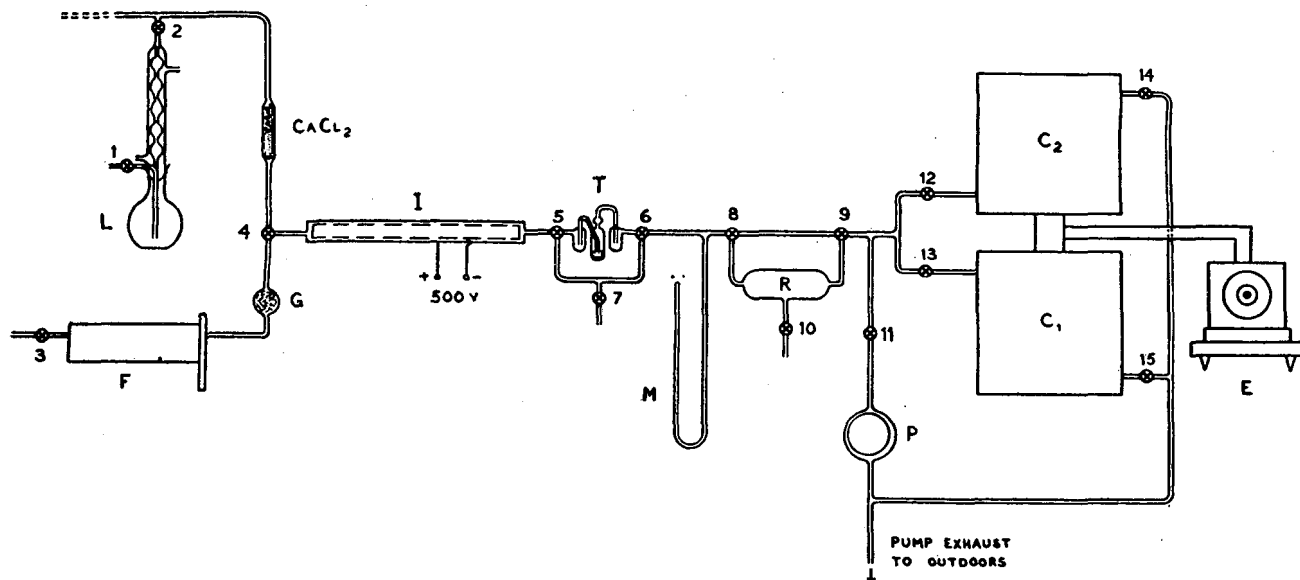


Figure 5. Apparatus for Determination of Radium

- | | |
|---|---|
| L. Sample flask | R. Reservoir |
| T. Mercury trap and valve | M. Manometer |
| F. Furnace | P. Pump |
| I. Ion trap (two insulated coaxial brass cylinders) | E. Recording electrometer |
| G. Glass wool bulb | C ₁ , C ₂ . Ionization chambers |

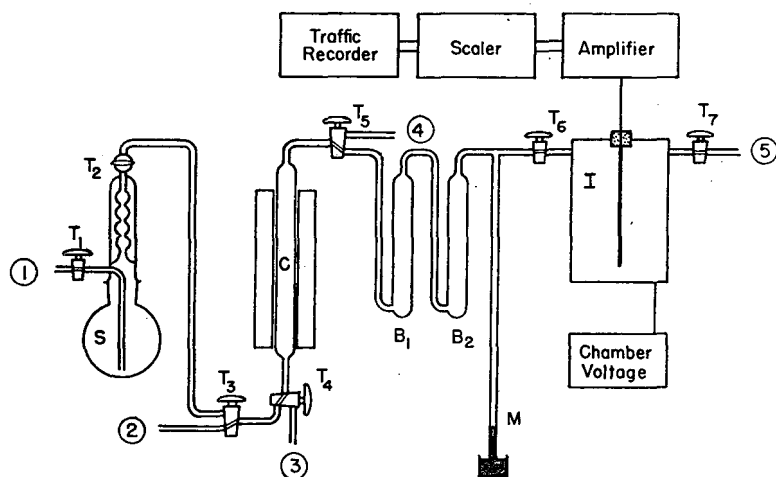


Figure 6. Apparatus for Determining Radium in Ores and Residues

- | | |
|---------------------------------------|---------------------------------------|
| S. Flask for standard radium solution | B ₂ . Phosphorus pentoxide |
| C. Reduced copper | M. Open mercury manometer |
| B ₁ . Drierite | I. Ion-counting chamber |

a reduced pressure of approximately 0.5 atmosphere while nitrogen is bubbled through it, usually for 17 to 18 minutes. The flask is then sealed off by stopcocks T_1 and T_2 , at atmospheric pressure, and the radon is allowed to collect until it is transferred to the chamber. The usual collection time that is convenient is of the order of 1 day. More radon is collected per gram of radium the longer the collection time, up to a practical limit of about 30 days.

The transfer of the radon is accomplished by reboiling in the same manner and allowing the nitrogen containing the radon to flow into the evacuated ion chamber. The nitrogen is purified by passing through hot reduced copper, C , to remove oxygen; through Drierite, B_1 , and phosphorus pentoxide, B_2 , to remove water vapor, and through Ascarite, B_1 , to remove carbon dioxide. The radon is allowed to come to equilibrium in the chamber for at least 3 hours and the count is usually made for 12 hours during the night when vibrations and voltage fluctuations of power lines are less prominent. The apparatus is calibrated against standard radium solutions.

β -Ray Methods. Because several of the elements of the uranium disintegration series have β -emission of high energy

(${}_{91}\text{UX}_2^{234}$ 2.32 m.e.v., 1.14 minutes; ${}_{88}\text{RaC}^{214}$ 3.15 m.e.v., 19.7 minutes) use has been made of this to determine uranium both after separating the active material and by counting without separation.

INDIRECT METHODS. The measurement of β - and γ -radiation from ores and minerals has been used to a considerable extent for estimation of uranium. It is possible by measuring the radiation from the material with and without absorption to obtain an indication of both the uranium and thorium content (29, 59).

The method of Chowdhuri (59) consists of an analysis of the absorption curve of the β -rays in aluminum. The method of Graven (29) consists in measuring the sample in an ionization chamber with an electrometer both with and without absorption by gypsum.

The Uranium and Related Materials Section of the National Bureau of Standards has used β -emission (in conjunction with γ -emission) for the analysis of ores in which equilibrium is known to have been reached. Chemically analyzed standards of similar nature are used

for comparison. When samples of varying density are examined, the absorption and geometry are affected considerably. It was found early that corrections for changes in density were not simple.

By compressing a 10-gram sample in a 2.5-cm. (1 inch) mold at 8 tons per square inch before counting, satisfactory results are obtained (41). The pellet is placed in the depression in D (Figure 7) and the knurled nut, F , is turned until the face of the sample is level with the top of C . The samples are then counted for a predetermined number of counts.

Table I indicates results selected at random.

DIRECT METHODS. The above-mentioned methods have been based on the assumption that radioactive equilibrium has occurred. Zemies and Hedvall (82) separated UX_1 from the sample and determined the β -radiation of the equilibrium amount of UX_2 which grows in a very short time. The method is independent of

Table I. Determination of Uranium

Chemical assay	U ₃ O ₈ , Per Cent	Count assay
0.228		0.225
0.455		0.459
0.91		0.91
2.73		2.64
0.866		0.896
1.179		1.211
12.61		12.52
16.51		16.69
20.94		21.01

Table II. Determination of Uranium

Chemical	U ₃ O ₈ , Per Cent	γ -Ray
18.69		18.61
13.90		13.76
35.48		35.75
29.76		29.57
1.34		1.37
0.56		0.56
0.29		0.28
0.027		0.029

radium concentration and of the history and treatment of the sample, except that the U-UX₁ equilibrium must have been established. This will be in about 3 months or less, depending on the previous treatment of the sample.

The sample is dissolved in nitric acid and zirconium nitrate is added as a carrier, after which the UX₁ and the zirconium are precipitated with sodium hypophosphate (Na₂H₂P₂O₆·6H₂O). The precipitate is transferred to an aluminum disk and counted. The method has been applied to minerals which contain 0.001 to 0.04% uranium.

If any chemical treatment of the material is necessary, it is generally simpler to finish the analysis by fluorescence or chemical means.

γ -Ray Methods. Uranium can be determined in ores in which it is in equilibrium by γ -count. The method is rapid and has proved applicable with ores containing 0.1 to 60% U₃O₈ but no thorium (48).

A constant volume of ground sample is used in the arrangement shown in Figure 8. Position I, II, or III is used according to the grade. Position I is for high-grade material, 35% U₃O₈ or over. A lead filter 2.5 mm. thick is permanently located between the counter and the brass support for the samples. Additional lead filters may be placed under the samples.

Samples of known uranium content are used as standards. Table II indicates results obtained with this method. In these materials there was a wide difference in densities.

For the measurement of large quantities of radium (order of milligrams) the gold-leaf electroscope still remains the best instrument. The method has been used at the National Bureau of Standards for years.

CHEMICAL DETERMINATION OF URANIUM

Uranium is usually determined more accurately by chemical than by radiochemical means. Therefore, if any chemical manipulation is necessary, it is usually advisable to finish by chemical means. A more complete résumé of this subject is given in the National Nuclear Energy Series (70).

Methods of Separation. It is only in rare cases that uranium can be determined without prior separation from interfering elements. In the course of his work the author has used primarily two methods of separation. In the first, uranium is extracted from a nitrate solution by using ether. In the second method impurities are separated from uranium before the element is determined by volumetric means.

The particular means chosen for the separation of uranium will depend upon such factors as the separation desired, the amount of uranium present, the nature and amounts of the accompanying

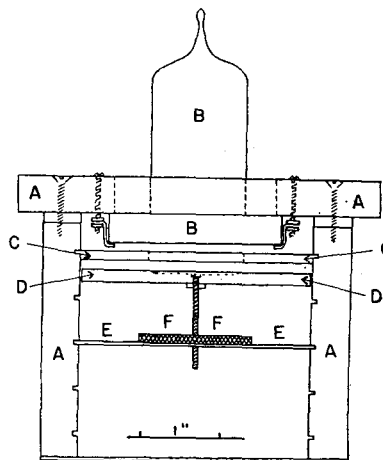
elements, the accuracy desired, and the effect of the reagents employed on the subsequent steps of the analysis. It is therefore impossible to evaluate the various methods categorically, for the discretion of the analyst is necessary in deciding on the best procedure for the analysis under consideration. Résumés (13, 67, 70, 75) of general methods of separation have been made.

Uranyl ion is precipitated by ammonium hydroxide along with iron, aluminum, and other members of the ammonium hydroxide group. However, in the presence of alkali carbonates it forms complex carbonates which are soluble.

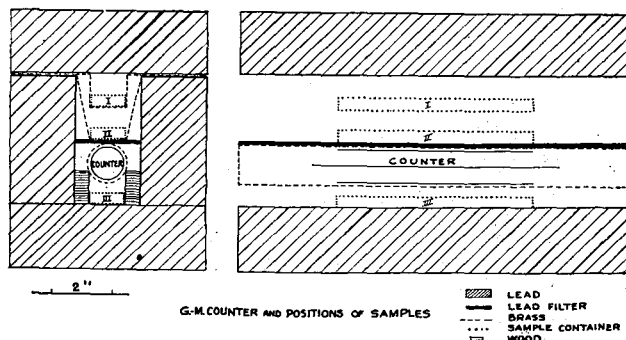
Gathering agents or carriers have been used in analytical chemistry for many years to collect a small amount of a precipitate distributed through a considerable volume of liquid (81). The carriers for uranium which have been used to the greatest extent to isolate traces of uranium for analytical purposes are ferric hydroxide and aluminum hydroxide.

The precipitation of uranium (IV) with cupferron is a very useful step in many analyses. The precipitate may be removed from the solution by extraction with an organic solvent as well as by filtration.

A number of other organic reagents are available for precipitation of uranium (VI). Each has its special uses. Thus, tannic acid precipitates uranium from carbonate solutions, while oxine (8-quinolinol) separates uranium as a compound that may be weighed, titrated, or extracted by a solvent. Quinaldic acid, insatin β -oxime, and 1-nitroso-2-naphthol each forms a precipitate which separates uranium from miscellaneous elements; they may be extracted with organic solvents as well as filtered.

**Figure 7. β -Ray Assembly**

- A. Lucite mount
- B. Mica window counter
- C. Aluminum plate with 1.25-inch hole
- D. Aluminum plate with 0.03-inch depression
- E. Aluminum plate with 0.16-inch hole
- F. Aluminum knurled nut

**Figure 8. γ -Ray Assembly**

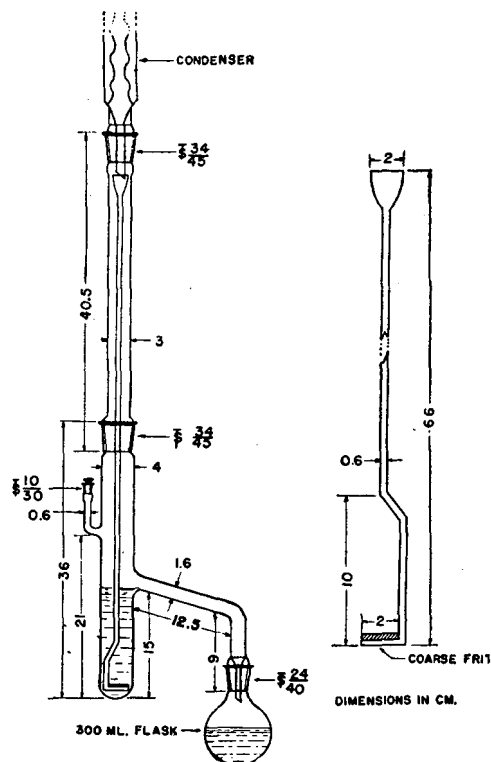


Figure 9. Continuous Extractor

One of the most useful complexes formed by uranyl salts is that with carbonates. Sodium peroxide has also proved effective for forming soluble uranium complexes. Other reagents that have more specialized applications in forming complexes of uranyl salts are hydroxylamine, citrate, and tartrate ions. One of the most common uranium (IV) complexes is with oxalates; citrates and tartrates form complexes over a wide pH range.

Extraction procedures in general give particularly clean-cut separations, and are highly recommended wherever their use is possible. With microamounts, extractions are usually more quantitative than precipitations. Ether extraction of uranyl nitrate is the most general procedure, while the extraction of various complexes finds special applications. These include chloroform or ether extraction of uranium (IV) cupferrate, aniline extraction of uranyl tannate, and chloroform extraction of uranyl complexes with antipyrine, oxine, etc.

Ions of the following metals are precipitated by cupferron from sulfuric or hydrochloric acid solutions (10%): iron, gallium, zirconium, columbium, tin, antimony, hafnium, titanium, vanadium, tantalum, and uranium (IV). The cupferrates of these elements are soluble in chloroform and thus can be extracted and removed from uranium (VI). Among others, the following elements are not precipitated or extracted: aluminum, chromium, beryllium, phosphorus, manganese, nickel, zinc, uranium (VI), boron (borate or fluoroborate), the alkaline earths, and the alkalis. The cupferron separation has been used chiefly as a means of separating interfering elements from uranyl solutions before volumetric analysis. Precipitation of uranium (IV) cupferrate (1, 39) has been used. Nitric acid should be absent in cupferron separation, and if precipitates are to be ignited, perchloric acid should also be absent. Sulfuric acid solutions are generally used but hydrochloric and organic acids can also be employed. The two valence states of uranium make possible the double cupferron procedure in which iron, titanium, etc., are precipitated or extracted from the remaining elements. It has been found necessary to have a reducing agent present in order to ensure complete precipitation of uranium (IV) cupferrate. Both hydroxylamine

(22) and sodium dithionite (44) have been used for this purpose. After the second step, the uranium (IV) cupferrate, $U(C_6H_5N_2O_2)_4$, may be either filtered or extracted with an organic solvent. The precipitate is flocculent and fairly easily washed.

The solubility of uranium nitrate in ether has been used for years for the separation of uranium from many elements (37, 65). Hecht and Grunwald (35) used ammonium nitrate as a salting agent to effect complete separation of uranium in the analysis of ores. Extraction is applicable to uranium-bearing materials of both high and low grade; the primary requisite is the complete conversion of the uranium to its nitrate. Both continuous and batch methods of extraction are successful. Continuous extraction, for which some modification of the Friedrich liquid extractor is employed, removes the uranium completely and efficiently. Figure 9 is the apparatus used at the National Bureau of Standards and is similar to the one described by Heberling (34). The side arm permits addition of nitric acid during the course of the extraction.

After being converted to the nitrate, the solution is transferred to a continuous extractor with the aid of an ammonium nitrate solution (700 grams of ammonium nitrate per liter of 10% nitric acid), and extracted with diethyl ether for 30 minutes. At this time, or sooner if the solution tends to hydrolyze, 10 ml. of ammonium nitrate-nitric acid solution is added. The aqueous phase is then stirred and the extraction is continued for another 30 minutes. The uranyl nitrate is now in the receiving flask, which was originally charged with 60 ml. of water and about 75 ml. of ether. The ether is removed after the extraction by evaporation on a steam bath or hot water bath and the solution is transferred to a beaker. To this is added sulfuric acid (1 to 1) and the solution is fumed twice to remove nitric acid. From this point a colorimetric or volumetric determination of the uranium may be made. If a volumetric method is used it may be necessary to make a cupferron-chloroform extraction to separate traces of impurities which may have been extracted.

The only elements that are extracted appreciably with uranium under the conditions used are cerium (IV) and thorium. In a volumetric determination, however, the presence of these elements is of no consequence when ceric sulfate is used in the titration. Ceric ion may be reduced to cerous with sodium nitrite before extraction. If the amount of vanadium is known to be under 1%, the error introduced by the amount that is extracted is not serious. With large amounts of vanadium the error may be minimized by evaporating the nitric acid solution to dryness. There is no effective way, thus far, of handling with certainty materials high in vanadium, although with materials high in vanadium the uranium may be removed with sodium hydroxide, using calcium hydroxide as a carrier prior to extraction (25). Iron, if in high concentration in the aqueous layer, may be extracted to a slight extent.

Interfering anions which may tie up the uranium or cause extraction of other elements must be either removed or treated in such a way as to effect complete recovery of the uranium. Chloride, for example, should be absent from the nitrate solution, as it interferes with the completeness of the extraction of uranium. Chloride causes certain other elements such as iron (III), etc., to be extracted. Up to 50 mg. of sulfate ion in 30 ml. of solution do not interfere. Large amounts interfere but can be made harmless by adding calcium ion. Phosphate has been found to decrease the distribution coefficient of uranium in an ether extraction. Apparently, once the uranium is precipitated as the phosphate, no more uranium will be extracted by the ether. Even 12% nitric acid will not redissolve uranyl phosphate. However, the higher the initial concentration of nitric acid the more uranium will be extracted before precipitation of uranyl phosphate occurs. A rather effective method of overcoming the influence of the phosphate ion, and also fluoride ion, consists in using ferric or aluminum nitrate, which serves to form complexes with these anions.

Methods of Determination. Gravimetric methods for uranium, require, in general, the absence or the prior separation of numerous other elements. They are used chiefly when macroamounts

of uranium are available. The normal weighing form is the oxide, U_3O_8 . This substance is formed upon proper ignition (900°C . in an oxidizing atmosphere) of any one of the following precipitates: ammonium diuranate, uranium (IV) fluoride, uranium dioxide, uranium peroxide, uranium (IV) oxalate, uranium (IV) cupferrate, uranyl oxinate, and many other precipitates formed by organic reagents.

Titration procedures are generally conceded to be the most satisfactory ones for the estimation of macroquantities of uranium. Microtitrations may be performed satisfactorily, but colorimetric or other optical methods are generally preferable for the estimation of small quantities of uranium. Methods based upon the prior reduction of uranium to the U (IV) state have been utilized most frequently. If uranium (III) is formed during the reduction, aeration serves to convert uranium (III) to uranium (IV) before titration. Although uranyl solutions can be titrated directly with standard titanous or chromous solutions, redoximetric procedures are rarely used because rigid precautions are required to preserve the standard reductants. It is usually easier to prepare tetravalent uranium and use an oxidimetric titration.

The reduction of the uranium is generally accomplished by means of zinc (43, 51) with occasional use of silver (5), chromous ion (46), or electrolytic methods (23), and ordinarily gives a mixture of uranium (III) and uranium (IV). With the exception of some potentiometric titrations the trivalent uranium is air-oxidized to the quadrivalent state. Quantitative reduction directly to the tetravalent state may be achieved with liquid zinc amalgam (60) or silver under certain controlled conditions. Amalgamated zinc in the form of a Jones reductor is the most convenient and widely used reductant. Nickel interferes with the reducing action of the Jones reductor (33). However, if a fresh portion of liquid zinc amalgam is used for each sample (53), there is less interference by substances that plate out in the amalgam.

The most common oxidizing agents used for titrating reduced uranium solutions are potassium permanganate (51), ceric sulfate (21), potassium dichromate (45, 73), and ferric sulfate (63). End points may be detected either by indicators or by electro-metric means. A precision of better than one part in a thousand may be obtained with any one of these oxidants in macrotitrations; however, with smaller amounts of uranium ($<10\text{ mg.}$) the errors increase. Below approximately 10 mg. small reductors and microburets should be used.

The choice of titrant depends on a number of factors, including speed of reaction at room temperature, possible objections to the addition of iron or phosphoric acid as catalysts, facilities for protecting hot solutions from air-oxidation, interfering substances, the stability of the titrant, and the accuracy desired. The only titration that proceeds to a satisfactory end point directly at room temperature without the addition of a catalyst is that with permanganate. With this oxidant chlorides must be absent, however, unless the usual solution of phosphoric acid and manganous sulfate is used. Furthermore, permanganate solutions are not so stable as those of dichromate or ceric sulfate. Titrations at room temperature with ceric sulfate or potassium dichromate in the presence of excess iron and/or phosphoric acid are satisfactory. In precision work, dichromate has the advantage of being a primary standard. Most titrations with ferric solutions must be made at elevated temperatures and therefore must be protected from air oxidation; but because large amounts of iron do not interfere, ferric titrations may be used for samples containing iron.

Electrometric titrations permit the accurate determination of the amount of overreduction in various solutions, and also the determination of several metals in the same solution, but are too time-consuming for most work. The ferric sulfate potentiometric method has been investigated (9) because it eliminates the interference of large amounts of iron.

Spectrophotometric and Colorimetric Methods. Of the inorganic reagents used for the colorimetric determination of

uranium, alkaline peroxide has the least interferences, and although not the most sensitive, has been most extensively employed. Rosenheim and Daehr (71) found that hydrogen peroxide when added to a uranyl solution made alkaline with sodium or ammonium carbonate gave a yellow color that varied directly with the uranyl ion content. Hackl (31) determined uranyl ion in sodium carbonate solution, using hydrogen peroxide. Cassidy (8) investigated the photometric determination of uranium as the nitrate, as the carbonate complex, and as the carbonate complex with peroxide. The conclusion reached was that the carbonate complex with peroxide was much more sensitive than the other two methods, but that the intensity of color increased with increase in amount of alkali carbonate and at the same time shifted the quality of color toward the red. Sodium peroxide and sodium hydroxide have been advocated (24) as giving more reproducible conditions and eliminating the interference of vanadium.

In all systems employing alkaline peroxide, whether sodium carbonate, sodium hydroxide, or ammonium hydroxide is used as the alkaline medium, chromium shows very serious interference. The correction for chromium by adding known amounts to standards has not proved satisfactory. The chromium may be removed by oxidation, followed by a double ammonium hydroxide precipitation, or by ether extraction of the nitrate solution after an ammonium hydroxide precipitation, or by electrolysis with a mercury cathode.

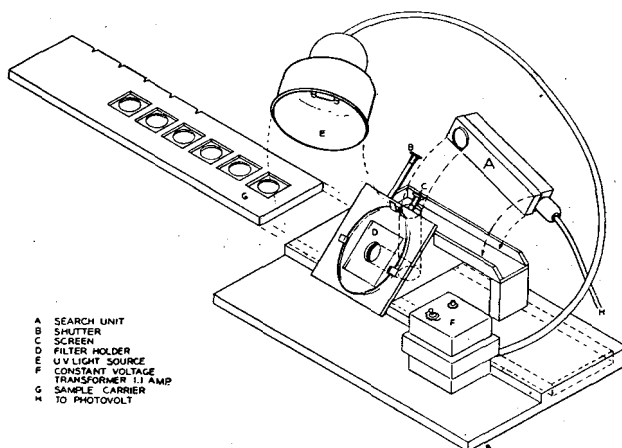


Figure 10. Fluorometer

Vanadium interferes to a marked extent in the usual procedure and cannot be compensated for by adding known amounts to standards. The results obtained in this manner are variable. When a sodium hydroxide-sodium peroxide system with high alkali content is used and the solution is brought to a boil and then cooled before photometric measurements, the effect of vanadium is eliminated (24). Vanadium cannot be completely separated by ether extraction and accompanies uranium to a marked extent in alkaline precipitations.

It has been observed (26) that some organic material is separated by the ether extraction and gives a color when sodium hydroxide and peroxide are added. It is therefore necessary to destroy organic matter, after the ether removal, by fuming with a mixture of nitric, perchloric, and sulfuric acids. Another source of interference is certain dilute hydrogen peroxides (3%) which give a yellow color when treated with alkali. This has not been found with the 30% hydrogen peroxide of commerce.

For general use the sodium hydroxide-peroxide or sodium hydroxide-sodium carbonate-peroxide system with the transmittancy measured from 400 to 430 $m\mu$ is preferred, as it is subject to less interference. Conditions are not so critical as in the sodium carbonate-peroxide system. For special cases the ammonium hydroxide-peroxide-tartrate system or the ammonium carbon-

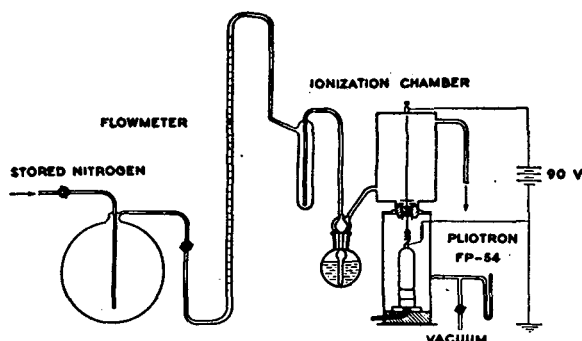


Figure 11. Apparatus of Thoron Method

ate-peroxide system may be preferred (74). The use of peroxide in acid solution has also been suggested (11).

Fluorometric Methods. Of all methods available for the determination of traces of uranium, the observation of the fluorescence is by far the most sensitive. The fluorescent properties of uranium when exposed to ultraviolet light were first pointed out by Stokes (76). Nichols and Slattery (62) found that the fluorescence was intensified by fusion with solids such as borax and sodium fluoride. The use of the latter compound permitted the visual detection of as little as 10^{-10} gram of uranium. Hernegger and Karlik (36) were the first to develop this fluorescent property into a quantitative analytical method. The method has been used extensively by Hoffman (38). The quenching of fluorescence by impurities in the sodium fluoride-uranium phosphor was described by Papish and Hoag (64).

Any ion or mixture of ions in the fluorescent disk or bead, which causes the apparent content as obtained by comparison with disks or beads of known uranium content to be less than the actual uranium content, is known as a quencher. The quenchers that may be frequently encountered are iron, chromium, copper, calcium, and silicon. By using an ether extraction of the nitrate the uranium can be removed from these and essentially all interfering elements.

The minimum quantity of uranium detectable by the fluorescent method of analysis is 10^{-11} gram of uranium in a phosphor made with a flux of 200 mg. of pure sodium fluoride (66).

Visual comparison with standards has been successful for uranium contents up to 50 micrograms. Through most of this range disks differing by less than 5% in their uranium content can be readily distinguished. The lowest level found useful is 0.01 microgram, though smaller amounts can be detected. The range recommended for visual comparison is from 0.1 to 2.1 micrograms; use of a longer range requires an inconveniently large number of standards. Photometric measurements have shown that the intensity of fluorescence is linear with the uranium content up to at least 50 micrograms.

Fluorometers (61, 66) such as that shown in Figure 10 (10) have proved highly successful for examination of the fused disks. The range of concentration that can be estimated depends on the instrument used.

THORIUM SERIES

The thorium series is shown in Figure 1.

Thorium is the important member of this series and for its radioactive determination thoron (${}_{86}\text{Th}^{220}$) and ${}_{84}\text{ThC}'^{212}$ are the most useful.

The determination of thorium by radioactivity methods is generally complicated by the presence of uranium. In monazite there may be 0.3% or more of uranium present. It is also necessary to have equilibrium established.

α -Ray Method. **INDIRECT METHODS.** The chief work in this field has been that of Evans *et al.* (16), who have described three methods.

1. Use of a vacuum tube electrometer to count all α -rays emitted from smooth surfaces of solids, such as polished rocks.
2. Counting all α -rays emitted from a powdered specimen, such as finely ground rocks or chemically prepared precipitates.
3. Counting of ThC' α -rays after exclusion of all shorter rays by absorbers placed over solid or powdered sources.

The third method reaches the thorium series directly. Methods 1 and 2 require correction of radiation due to the uranium series. The best results appeared to have been obtained with method 2.

DIRECT METHOD. The thoron method of Urry (80) and Goodman and Evans (27) involves chemical manipulation.

The sample is fused, the silica removed, and final solution made in hydrochloric or nitric acid. The solution is then placed in the apparatus as shown in Figure 11 (23) and nitrogen is swept through. A definite fraction of the thoron atoms disintegrate in the chamber and the deflection of the galvanometer connected to the FP-54 tube is measured photographically.

This method is much longer than method 2 and evidently is not as satisfactory.

β -Ray Method. Although β -ray methods have been used, they have about the same disadvantages as with uranium (29).

γ -Ray Method. By use of very sensitive γ -ray tube counters and larger sources, it is possible to detect the feeble γ -rays emitted. This method has been used by Evans *et al.* (16).

Taken all in all, the methods for the determination of thorium by radioactivity measurements have not been so satisfactory as with uranium, where the radon can be readily isolated and determined.

Chemical Determination of Thorium. A complete résumé of the determination of thorium is given in the "National Nuclear Energy Series" (69) and by Moeller *et al.* (58). In general, the analytical chemistry of thorium is more difficult than that of uranium. Thorium, having only one valence, cannot be determined by oxidation or reduction processes and therefore precipitation methods are usually employed.

METHODS OF SEPARATION. Organic reagents are not of general use in the separation of thorium because so many other elements are precipitated with it. An exception occurs when thorium is present in an alloy containing in addition only metals not precipitated with it. Complexes of thorium such as are found useful in the uranium separations are not widely employed. The usual citrate and tartrate complexes are sometimes used to hold the thorium in alkaline solutions. Extraction procedures have not been widely employed, although chloroform can be used to extract other cupferrates in an acid solution, leaving thorium which can be extracted at pH 9 in a carbonate-citrate solution and separated from uranium in this manner (32).

The separation of thorium from the rare earths has received detailed attention, and several methods of precipitating thorium hydroxide without precipitating the rare earth hydroxides have been employed. By the proper choice of reagents it is possible to change the pH of a solution gradually, so that thorium hydroxide will precipitate. Thorium hydroxide begins to precipitate about pH 3.3 and precipitation is complete at about pH 6, whereas most of the rare earths do not start to precipitate until pH 6.5 is reached (6). Potassium azide effects this separation, and when a thorium solution is boiled with this reagent the latter is hydrolyzed, and thorium hydroxide is quantitatively thrown down, while hydrazoic acid is boiled away (14). Sodium thiosulfate accomplishes the same end, but one or more reprecipitations are required for complete separation from cerium; only a partial separation from uranium is made (20, 68). Aluminum, scandium, titanium, and zirconium are also precipitated. The thiosulfate procedure has been used for years as an analytical method (56). Hexamethylenetetramine causes the preferential precipitation of thorium hydroxide, separating it from the rare earths (42). When present in large amounts, the rare earths may partially come down and may require a second precipitation. The hexa-

methylenetetramine procedure has been used extensively for the separation from the rare earths and is satisfactory.

The peroxide is gelatinous from a neutral solution and has a tendency to be transparent; from a slightly basic solution it is not so gelatinous and has a lower peroxide content; from an acid solution it is most nearly completely precipitated at elevated temperatures, is opaque, and is more readily filtered. Because few elements are precipitated in acid medium, it is preferred. If precipitated from a too weakly acid solution, the product is of the same nature as the less crystalline variety.

The separation of thorium as the oxalate is a classical method and is widely employed. In the common gravimetric procedures for thorium, the oxalate is precipitated and ignited to the oxide. The oxalate precipitation method is frequently used because it can be carried out in acid solution and thorium is thus separated from many other elements. Zirconium has a tendency to precipitate with the thorium, but can be kept in solution with an excess of oxalate. Enough oxalate must be added to satisfy the oxalate-complexing ions (uranyl, ferric, etc.).

The separation of thorium from other elements through the iodate (55) is most popular because of the excellence of the separation, the rapidity of filtration of the crystalline precipitate, and the ease of re-solution. The method has been in use for years. For macroamounts the reaction is carried out in about 6 *N* nitric acid solution. For traces, the solutions should be 0.5 to 1 *N* nitric acid, as considerable loss of thorium is entailed at higher acid concentration. An excess of iodate reduces the solubility of the thorium iodate. Separations are not made from zirconium and titanium, which constitute the only serious interferences. Cerium (IV) and uranium (IV) are also precipitated by iodate, but if the solution is pretreated with hydrogen peroxide the former is reduced and the latter is oxidized, and their precipitation is avoided. In the presence of appreciable amounts of rare earths, repeated precipitations may be necessary.

Hydrofluoric acid precipitates the somewhat gelatinous and highly insoluble fluoride, $\text{ThF}_4 \cdot 8\text{H}_2\text{O}$, from thorium solutions. Although not suitable for quantitative work, certain separations are possible which give this method some importance. The reaction is carried out in acid solution. Centrifuging rather than filtering is desirable. Small amounts may be readily filtered when collected with mercurous chloride (30). Thorium is separated from zirconium (72); the excess fluoride forms the soluble fluo-zirconate ion, while thorium is precipitated. Hafnium behaves similarly. This serves to separate thorium from those elements forming soluble fluorides or complexes with fluorides including columbium, tantalum, and tungsten.

Benzeneearsonic acid (phenylarsonic acid) precipitates titanium, zirconium, hafnium, and thorium, as well as a few other elements [such as tin (IV), columbium, and tantalum]. The titanium, zirconium, and hafnium may be precipitated from strongly acid solutions, but thorium requires a buffered acetate medium (67). The precipitate is easily filtered and washed. The rare earths are coprecipitated to some extent with thorium benzeneearsonate and a double precipitation is usually necessary. Cerium (IV) and uranium (IV) are also precipitated.

Several derivatives of benzeneearsonic acid have been employed (19). For microgram amounts *p*-dimethylaminoazobenzeneearsonic acid (parasonic acid) has been satisfactory (7, 30) and has been employed in a colorimetric method for determining thorium (30). In one procedure the precipitation is carried out in solutions of pH 1 to 2. It has been stated that zirconium may be separated by a prior treatment with the reagent (7) in a highly acid solution.

METHODS OF DETERMINATION. The methods of determining thorium are predominately gravimetric, involving ignition to thoria and weighing. This is the method ordinarily preferred when only a few samples are to be analyzed, and is the most accurate. Ordinarily, one precipitates the thorium as the hydroxide, peroxide, or oxalate, and ignites to the dioxide. The titri-

metric methods are most useful when numerous samples are to be analyzed but usually involve considerable preliminary separation; the technique involving the precipitation of thorium molybdate, followed by reduction and titration of molybdenum has been used to advantage when no interfering elements are present (2, 54). The titration of iodine from $\text{Th}(\text{IO}_3)_4$ or $\text{KIO}_3 \cdot 4\text{Th}(\text{IO}_3)_4$ has been employed to a limited extent for amounts of thorium from 5 to 50 mg. (52).

The procedures for the determination of traces of thorium (up to about 1 mg.) are relatively few. Because the ion is colorless, the methods depend upon the formation of a colored derivative, or a compound from which a color may be developed. The reagents 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulfonic acid and parasonic acid have been used with some success. The *m*-nitrobenzoate has been used by reducing to the corresponding amino compound which is colored.

The highly insoluble and highly colored thorium derivative of *p*-dimethylaminoazobenzeneearsonic acid (parasonic acid) may be precipitated, filtered or centrifuged, washed, and treated with ammonia or sodium hydroxide (30). The color of the solution formed may be measured with a spectrophotometer. The method is applicable for amounts of thorium in the range of 0.5 to 500 micrograms, and by proper choice of size of sample and cuvette the limits may be varied widely. The compound 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulfonic acid forms a strawberry-red precipitate with thorium salts (47), and this serves as the basis of a colorimetric determination. It can be used without separation from the excess reagent (77), but the absorption bands are such that the amount of reagent must be carefully measured and an approximate knowledge of the thorium range must be known. The method has been used for the determination of microgram quantities of thorium, and the color is stable at least 24 hours. The best pH range is 0.3 to 1.

When thorium iodate is reduced with hypophosphorous acid in the presence of sulfuric acid, iodine is liberated (18). The iodine may be titrated or, if the reaction takes place in carbon tetrachloride, the color of the carbon tetrachloride solution may be measured. Because the measurement is indirect, it is essential that the thorium iodate be free of any other iodate.

Quantities of thorium less than 1 mg. may be estimated nephelometrically as thorium iodate (30). The thorium, separated from interfering ions, is treated with an excess of potassium iodate and compared with standards prepared similarly. The method is rapid and is suited for certain routine work.

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Nucleonics and Analytical Chemistry Symposium

METHOD OF ACTIVATION ANALYSIS

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THE phenomenal growth of nuclear science during the past decade and a half has been replete with important consequences for all the natural sciences. Analytical chemistry, and particularly the discipline of inorganic analysis, has been especially favored by this development. Among other things, a new technique for the detection of impurities in materials by forming their artificially radioactive isotopes has become possible. This novel procedure, which may be termed "the method of radioactivation analysis," or, more succinctly, "activation analysis," is foremost a method for the determination of minute quantities of foreign constituents by reason of the very great sensitivities attainable in the detection of radioactivity. The procedure is unusually free from interferences by other elements by virtue of the unique decay periods of their artificial radio-

activities and of the radiations they emit. Likewise, the danger of contamination during the course of the analysis, which is an ever-present hazard in conventional trace determinations, is almost completely absent. Finally, the physical basis for the method appears to be very broad, for now the phenomenon of artificial radioactivity has been shown to be widely spread throughout the periodic table. Among the 96 elements, over 700 radioactive species have been established at the present writing, and the number of radionuclides appears to increase almost daily.

Several applications of the method of activation analysis have been described since the discovery of artificial radioactivity in 1934. Perhaps the earliest among these examples were those reported by Hevesy and Levi (15) and by Seaborg and Livingston

Nuclear science has developed to the point where a new method of analysis for the detection of impurities by forming their artificially radioactive isotopes has become possible for a wide variety of elements. Remarkable sensitivity may be attained on occasion by use of the cyclotron or the chain-reacting pile. A comparative procedure wherein internal standards are employed is to be recommended in practice, although in principle the absolute quantity of the element sought may be computed directly from the

measurements. The feasibility of applying the method should be determined by a prior consideration of the relevant established nuclear data. The means for nuclear excitation, the kind of instrumentation best suited for radioactivity detection, and the necessity for chemical separations are of especial importance. The widespread use of activation analysis appears to hinge in a decisive fashion upon the emergence of machines of relatively modest cost for laboratory production of artificial radioactivity.

(32). The former authors made use of the relatively strong activities produced in dysprosium and in europium when these elements captured slow neutrons to estimate the extent to which they were present in rare earth mixtures. A comparison of the intensity of the distinctive 2.4-hour period of dysprosium, formed in the irradiation of impure yttrium samples, with the intensities produced in dysprosium-yttrium mixtures of known composition, for example, allowed the estimation of as little as 0.1% dysprosium contamination. A direct estimation of europium occurring in 1% concentration in a gadolinium preparation was accomplished in a similar manner. The avoidance in this work of the traditionally difficult chemical separation required when conventional analytical methods are applied to rare earth analysis is of especial interest. In their work at the 36-inch Berkeley cyclotron, the latter authors demonstrated that very small amounts of gallium contamination in otherwise highly pure iron could be detected after bombardment of the iron with 6.4-m.e.v. deuterons. In this case, the estimate of 6 parts per million of gallium impurity was based on what seemed to be a reasonable assumption for the magnitude of the cross section, or probability of the reaction of the gallium nucleuses with fast deuterons.

More recently analogous investigations have been described by King and Henderson (20), who report the detection of as little as several hundredths of 1% of copper in pure silver by means of the reaction of 16-m.e.v. α -particles with the copper impurity [$\text{Cu}^{63}(\alpha, n)$ 9.4-hour Ga^{66}] to produce radiogallium, and by Sagane and co-workers (30) who employed 3-m.e.v. deuterons to reveal the presence of 10 p.p.m. of sodium in aluminum. An excellent, detailed example of the use of energetic charged particles in activation analysis may be found in a paper by Ardenne and Bernhard (3) on the determination of carbon in steel, using 0.8-m.e.v. deuterons produced by an electrostatic accelerator. A procedure for the very rapid determination of carbon down to a concentration of 0.05% was established.

Although it might seem that smaller amounts of impurities can be detected when energetic charged particles rather than neutrons are employed, in actuality this is by no means the case. Following the advent of the chain-reacting pile about 6 years ago, fluxes of slow neutrons millions of times larger than those used by Hevesy became available to the chemists associated with the American nuclear energy project. As a consequence, since late 1943 at the Oak Ridge National Laboratory, analysis by means of radioactivation has become an everyday procedure for the determination of impurities in a wide variety of pure chemicals, in metals and alloys, and even in organic substances. The technique has been particularly valuable since 1946 in connection with the production of radionuclides for the Atomic Energy Commission radioisotope distribution program. Here, it is used as a guide in the selection of pure elements or compounds for pile bombardment, or as a control in purification operations for the preparation of these materials.

Relatively few examples of the enormous sensitivity inherent in procedures which employ the pile as an analytical tool have

appeared in the literature thus far. In a number of cases it has been possible to determine the quantities of constituents present in concentrations far below the limits of ordinary spectrochemical sensitivity. For example, less than one part per billion of iridium may be detected in the best commercial grades of pure platinum metal. In connection recently with rare earth separations by means of the technique of ion exchange chromatography (19) the presence of as little as 10 p.p.m. of thulium in spectrochemically pure erbium sesquioxide was demonstrated after the irradiation of a sample in the pile and the isolation of the rare earth impurities. Later in a special investigation of the method of activation analysis, Clark and Overman (11) showed that a manganese contamination as small as 0.6 p.p.m. could be detected in samples of ultrapure commercial hydrous aluminum oxide. The employment of modern high intensity sources of slow neutrons for the estimation of microamounts of gallium and palladium in meteorites (8), and for the analysis of the microcomposition of biological tissue (37) has been reported within the past year also.

A number of considerations have made it appear that the method of activation analysis ultimately may find widespread application. The somewhat primitive state of development of this new technique will be recognized immediately, however, from the illustrative examples cited.

PRINCIPLES OF THE METHOD

The sample to be analyzed is placed in a homogeneous flux of energetic charged particles or fast or slow neutrons for a length of time sufficient to produce a measurable amount of a radioisotope of the element to be determined. The rate of growth of the number of the radioactive atoms, N^* , with time is given then by the well-known equation (26):

$$dN^*/dt = f\sigma_{ac}N - \lambda N^* \quad (1)$$

which upon integration over the irradiation interval yields:

$$N^* = \frac{f\sigma_{ac}N}{\lambda} (1 - e^{-\lambda t}) \quad (2)$$

In these equations, f is the flux of bombarding particles in units of particles per square centimeter per second; σ_{ac} is the isotopic cross section for the nuclear reaction in units of square centimeter per target atom; N is the number of target atoms; and λ is the radioactive decay constant which is connected with the half-life, $T_{1/2}$, by the relation, $\lambda = 0.693/T_{1/2}$.

The amount of activity, A_t , in units of disintegrations per second, exhibited by the atoms N^* produced up to a time, t , is given by the expression:

$$A_t = \lambda N^* = f\sigma_{ac}N(1 - e^{-\lambda t}) = A_{\infty} \left(1 - e^{-\frac{0.693 t}{T_{1/2}}}\right) \quad (3)$$

The product $f\sigma_{ac}N$ in Equation 3 may be taken as the saturation activity, A_{∞} , for evidently it is the activity produced by an infinitely long irradiation. The factor within the parentheses may be termed the "saturation factor," S , which is seen to vary

between zero and unity. Simply, for the case covered by Equation 1, the activity produced up to any time, A_t , is given by the product of the saturation activity and the saturation factor.

The utility of the foregoing equations will be determined by the extent of the applicability of the suppositions made in their derivation. In the deduction of Equation 1 it was assumed, for example, that the rate of formation of radioactivity, given by $f\sigma_{ac}N$, was constant during the irradiation interval. Such a condition of necessity implies that the flux of charged particles or neutrons through the sample is constant with time. Furthermore, the average energy of the particles making up the flux was assumed to be constant, as the activation cross section, σ_{ac} , is a function of this energy and will be constant only for constant energy. Finally, the original number of target atoms must not decrease perceptibly with time owing to their consumption by the nuclear reaction. Evidently, this latter possibility will depend upon the magnitude of f and σ_{ac} , whose product, fortunately, is almost never sufficiently large to give concern because of this complication. If the foregoing conditions can be satisfied experimentally, Equations 1 to 3 will describe the growth of a single radioactive species up to the time of the end of the bombardment, t . Subsequently, the activity, A_t , so formed will decay with its characteristic half-life, so that the amount of radioactivity in the sample, A_t' , at time t' after the bombardment will be given by:

$$A_t' = A_t e^{-\lambda t'} = A_{\infty} e^{-\lambda t'} (1 - e^{-\lambda t}) \quad (4)$$

Sometimes the decay may give rise to a daughter radioactivity rather than to a stable nuclide. If the half-life of the daughter be appreciably shorter than that of its parent, the total activity will be observed to increase immediately after the bombardment. The quantitative description of this and of other types of chain relations may be found in the authoritative treatise by Rutherford, Chadwick, and Ellis (29).

A discussion of the factors that determine the sensitivity of the method of activation analysis may be facilitated by writing Equation 3 in the form:

$$\text{Grams of element of natural isotopic composition} = \frac{A_t \times M}{6.02 \times 10^{23} \times f\sigma_{ac}(1 - e^{-0.693t/T_{1/2}})\theta} \quad (5)$$

where M is the chemical atomic weight of the element sought, θ is the fractional abundance of the target isotope in the naturally occurring element, and the other symbols have the meaning previously assigned. To detect a very small mass of a desired element according to Equation 5 it is necessary: that the flux be large; that the activation cross section be large; that the radionuclide formed possess a short half-life; and preferably that the element be of low atomic weight and contain the target isotope in high relative abundance.

The character of the radiations emitted in the decay of the radioisotope, and the conditions under which the measurements are made also play an important role in determining the sensitivity in a given instance. Thus, for example, the observed counting rate, C^β , for β -particles measured with a Geiger-Müller counter may be related to the rate of emission of particles, A_t^β , by the equation:

$$C^\beta(\text{counts per second}) = A_t^\beta \epsilon (G/100) f_A f_s \quad (6a)$$

$$C^\beta/A_t^\beta = Y \quad (6b)$$

where

- ϵ = intrinsic counting efficiency of the detector for the radiations being measured—i.e., the ionization probability for particulate or for quantum radiations
- G = the geometry, or the fraction of the solid angle enclosing the source subtended by the sensitive volume of the detector
- f_A = factor for the effect of the absorption of the radiations in the wall of the detector, in the air between the source and the detector, in the source itself, etc.

f_s = factor for the effect of scattering—viz., forward scattering in the source, and from the surroundings, back-scattering from the source mounting, etc.

Y = counting yield, or ratio between the counting rate due to a certain type of particle and the rate of emission of the particles by the source being measured (16)

It may be seen from Equation 6 that the ratio between the counting rate and the particulate emission rate will be determined by the product of four separate factors:

When β -particles are detected with conventional type Geiger-Müller counters, ϵ is very close to unity over a wide range of energies. The counting efficiency for quantum radiations, however, is generally much smaller and is energy-dependent. With x-rays, values of ϵ as high as 0.1 can be obtained by special gaseous filling mixtures; usually, however, values between a fraction of 1% and several per cent are observed. Efficiencies of the same order of magnitude and even somewhat lower are found with γ -radiations (14). The geometry factor, G , is somewhat less than 0.5 when solid radioactive samples are assayed using mica end-window Geiger-Müller counting tubes. If the radioactive species is a gas which may be made to fill the detector, values of G can be made very close to unity. The absorption factor, f_A , is almost always appreciably smaller than unity, particularly in measurements of low energy β -radiation. In such cases every precaution must be taken to minimize absorption effects as, for example, by using virtually weightless samples, thin-window or windowless counters, etc. The contribution from the scattering of radiations differs from those just mentioned in that f_s may exceed unity, sometimes attaining a value as large as 1.75 when energetic β -emitting samples are mounted above high atomic number materials such as platinum.

It is not possible here to give a description of the procedures for the exact evaluation of the counting yield factor even in the important case of β -counting. Fortunately, this topic has been the subject of recent careful systematic investigations (43), which have demonstrated that A_t^β can be evaluated with a probable error of 2 to 4% for radionuclides having maximum β -energies between 0.3 and 1.0 m.e.v. and to within 2% (or less) for greater energies. In view of the wide variation in ϵ , depending upon whether the radioactivated nucleus decays with the emission of β -particles, x-rays, or γ -rays, it is seen that the greatest sensitivity in activation analysis will be attained when the first of these radiations is measured, unless specialized detecting equipment is employed (9). The conclusion to be drawn from these necessarily brief remarks is, then, that the type of detecting equipment employed and the technique of assay, including sample preparation and mounting, will be determined by the radionuclide utilized for analysis.

It is to be pointed out finally in regard to Equation 5 that the absolute mass of the constituent to be determined may be estimated if, in addition to a knowledge of the absolute disintegration rate, A_t , the absolute magnitude of the flux, the reaction cross section and half-life are known. No signal difficulty has appeared to beset the determination of the latter two of these quantities, fortunately, and increasingly more accurate values are continually appearing in the literature (33, 40). Accurate measurements of the flux, however, pose many problems, especially for beams of energetic charged particles such as protons, deuterons, and α -particles from cyclotrons, etc. Procedures for the measurement of the absolute value of the thermal neutron density created by a radium-beryllium source embedded in a thick layer of paraffin have been described (2).

If Equation 5 is to be used to estimate the absolute mass, a further caution deserves to be stressed. The observed counting rate will be related by Equation 6 to the true or absolute radioactive disintegration rate only if the β -spectrum is simple—viz., one β -particle per disintegration—or, if only one x-ray or γ -ray is emitted per disintegration. Otherwise, the net counting yield, defined as the ratio between the total counting rate due to the disintegration of the radionuclide and its true disintegration rate, must be used. The net counting yield thus takes the various possible disintegration modes into account.

For example, if a hypothetical nucleus decays 25% of the time with the emission of a 1.5-m.e.v. β -ray and 75% with the emission of a 0.6-m.e.v. β -ray followed by a 0.9-m.e.v. γ -ray, and if for the experimental arrangement employed the counting yield, Y , of the detector is 0.23 for a 1.5-m.e.v. β -ray, 0.11 for a 0.6-m.e.v. β -ray, and 0.02 for a 0.9-m.e.v. γ -ray, the net counting yield will be $(0.25 \times 0.23) + (0.75 \times 0.11) + (0.75 \times 0.02) = 0.155$.

Clearly, the determination of the net counting yield depends upon information concerning the decay scheme for the radionuclide measured. At the present time, the development of the field of nuclear spectroscopy is such that probably not more than several dozen reliable disintegration schemes have been established among the 700 or more radionuclides known to exist. Here again, this branch of nuclear science is undergoing an intensive development and the accurate characterization of new isotopes is proceeding with great rapidity. The growth of this branch of nuclear science is of the greatest import for nuclear chemistry, because use of radioactive substances for absolute physical and biological measurements is dependent upon a complete knowledge of the disintegration modes.

Fortunately for the application of the method of activation to problems of chemical and isotopic analysis, it is not necessary that the difficulties just mentioned be overcome. Good accuracy in the analysis of unknowns can be realized by a procedure involving comparative measurements with samples of known composition. These standard samples, which should be of the same general composition as the unknown, are subjected to an irradiation in an arrangement identical with that for the unknowns, and, if possible, at the same time. As in radioisotope tracer methodology, identical chemical operations are carried out on the known and unknown samples, and the aliquots prepared for the radioactivity assay should be mounted so as to be as nearly alike as is possible with respect to backing and sample spread. The counting rate should be measured with the standard in the same position with respect to the detector as the unknown. A comparison of these two counting rates, corrected to the same time if decay is important, then makes possible an estimate of the weight of unknown as follows:

$$\frac{(\text{Total activity from element } X \text{ in unknown})}{(\text{Total activity from element } X \text{ in standard})} = \frac{\text{mass of } X \text{ in unknown}}{\text{mass of } X \text{ in standard}} \quad (7)$$

If a number of samples containing varying amounts of unknown are to be dealt with on a routine basis it may be desirable to construct a calibration curve using a series of internal standards. Frequently, however, one properly chosen standard sample will be sufficient for the conduct of a given analysis.

When the element to be determined is present only in trace quantities it is generally desirable to add a small known amount of the naturally occurring element to the sample after irradiation to serve as a "carrier" to facilitate the chemical isolation of the desired radioactive species. Generally solid compounds containing the radionuclides are preferable, the chief specification being purity and definiteness of composition. The ratio of the weight of the aliquot counted to the initial weight of added carrier determines the chemical yield of the separation and purification operations. The observed counting rates for the unknown and the standard samples may be corrected for chemical losses using the chemical yield figures then, if these differ appreciably. Differences in the total weights of the assay compounds isolated from the unknown and standard samples may necessitate corrections also for differences in the self-absorption of the radioactive radiations emitted. This correction, best determined empirically, will be important if β -emitters of low energy are to be measured (22).

Assuming that the various correction factors mentioned can be determined with requisite accuracy, and that the treatment of the standard sample and the unknown has been as nearly identical as possible, the chief source of uncertainty in a result obtained by

the comparative method will be the uncertainty in the counting rate determinations. A discussion of the estimation of the random errors in counting rate determinations resulting from the statistical nature of radioactive decay may be found in another paper in this symposium (21). Somewhat limited experience appears to indicate that an over-all accuracy better than $\pm 10\%$ may be achieved without difficulty in the analysis of unknowns for trace constituents.

The comparative method of activation analysis may be epitomized as follows:

Irradiate a sample of the substance to be analyzed together with a standard sample containing a predetermined weight of the element to be determined. Dissolve the samples and add to the solutions a known weight of the element whose radioactivity is to be measured. Chemically process the added element so as to free it from the bulk constituents in the sample and to remove quantitatively any contaminating radioactivities produced in other elements present in the unknown. Determine the chemical yield of the procedure. Compare the activity from the unknown with that from the standard. As a check on the radiochemical purity of the assay samples it may be desirable to measure their half-lives and to characterize their radiations by means of aluminum or lead absorption curves, or otherwise.

CURRENT FEASIBILITY OF METHOD OF ACTIVATION ANALYSIS

The importance of the method of radioactivation for analytical chemistry appears to be as a procedure for trace analysis of wide generality which can be made to give, on occasion, unequaled sensitivity in detection. The degree to which this new method will find widespread use for analysis almost certainly will depend upon the future general laboratory availability of the tools of nuclear science for the production and measurement of radioactivity. At present it would seem that the latter aspect of this problem is in a satisfactory state of development. Equipment is now procurable commercially for the efficient detection and measurement of nearly all the types of radiations given out in radioactive decay. During the past three years, new basic instrument designs of demonstrated performance and reliability have appeared, some of which have originated at the Oak Ridge National Laboratory (6). Further instrumentational evolution directed towards simplifying radioactivity measurements to an almost wholly mechanical routine will be desirable, and indeed, there is indication that such a trend is in progress.

Machines for the laboratory production of radioactivity on a scale to be of value for analytical and preparative purposes appear, on the other hand, to be in a rudimentary stage of advancement. Perhaps the desired technical development in this direction could be stimulated if a decision as to which type of nuclear projectile, slow neutrons or energetic charge particles, should be employed to give the more economical laboratory scale synthesis of radioactivity. It will not be possible here to give more than abbreviated discussion of this subject, from the standpoint of the needs for activation analysis.

The obvious criteria of sensitivity and convenience may be used to decide on the feasibility of the method of activation analysis for the estimation of a given element in a given matrix. For example, generally it will not be convenient to analyze by means of radioactivation when only radionuclides of long half-life may be formed from the element sought, for in this case, as may be seen from Equation 5, in order to attain good sensitivity prohibitively long bombardments will be required. If a very large flux of nuclear particles can be brought to bear on the sample, and/or if the nuclear reaction cross section is large, adequate sensitivity may be realized even with short irradiations. As a rough guide, however, it is desirable that the generated radioactivity exhibit a half-life between 3 minutes and 100 hours. Because on the average there are approximately three radioactive isotopes for every stable isotope in the periodic table, in actual practice a limitation because of the lack of a suitable radioactive indicator is not likely to prove serious. The feasibility of the method then, in so far as this is determined by the sensitivity is seen to be dependent prin-

cipally on the flux and on the reaction probability. These latter quantities are not altogether unrelated, as the magnitude of the activation cross section, σ_{ac} , will determine the flux required for a given sensitivity.

The character and magnitude of the flux required will determine the type and size of the nuclear machine in turn. Accordingly, it will be of interest to examine how σ_{ac} varies with the nature and energy of the bombarding nuclear projectile. These detailed considerations may be introduced best by a definition of the concept of activation cross section, σ_{ac} :

Consider a thin layer of material containing N nuclei per square centimeter to be acted upon by a flux of f elementary particles per square centimeter. If it is determined that N' target nuclei are involved in a reaction forming a radionuclide, the activation cross section, σ_{ac} , for the reaction is defined by the equation:

$$N' = f\sigma_{ac}N \quad (7)$$

In this definition it is assumed that the target is thin enough so that any change of f with the penetration may be neglected.

Because nuclear reactions may be regarded as collisional processes to a first approximation, the reaction probability might be expected to be proportional to the geometric area presented by the target nucleus. Thus, cross sections of the order of 10^{-24} sq. cm. per atom, or less, would be anticipated, and, in fact, are observed. The target nucleus, of course, carries a positive charge, $+Ze$, which acts as a barrier preventing effective collisions with charged bombarding particles. Particles such as protons, deuterons, and helium nuclei for this reason must be accelerated until they possess sufficient energy to combine with the target nucleus. Although the variation of the yield of nuclear reactions with energy for charged particles can be predicted only from an intimate knowledge of nuclear binding energies, potential barriers, competing reactions, and other factors discussed in detail elsewhere (4, 5, 23), certain very general features of significance for the production of artificial radioactivity may be mentioned. Reactions involving charged particles show either a very small or zero cross section below a fairly well defined threshold energy which increases with the atomic number of the target nucleus. The yield of the reaction above this threshold increases almost

exponentially with energy, following the probability of penetration of the nuclear potential barrier. The cross section tends to approach the geometric area of the nucleus approximately at still higher energies and then either to remain constant, or to decrease, owing to the onset of new and competing nuclear reactions. An example of a reasonably typical cross-section, energy curve, known as an "excitation function" is given in Figure 1 for the reaction of energetic deuterons with sodium to form the well-known 14.8-hour Na^{24} radionuclide (12). Deuteron reactions generally show higher yields than proton or helium ion reactions for equivalent ion energies. The superiority of the deuteron as a nuclear transformation agent arises in part as a consequence of the fact that generally neutrons are among the reaction products. Reactions having charged particle products are usually less probable than those producing neutrons, for the former must penetrate the electrostatic potential barrier of the compound nucleus in order to be emitted.

The interaction of bombarding neutrons with target nuclei according to these views should occur as easily at low as at high

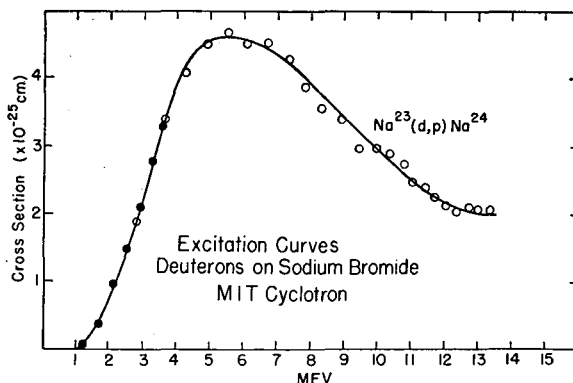


Figure 1. Excitation Function for Production of 14.8-Hour Na^{24} Activity by Cyclotron-Accelerated Deuterons

Data adapted from Clarke and Irvine (12)

Table I. Summary of Atomic Activation Cross Sections for Thermal Neutron Capture

		(Values $\times 10^{24}$ sq. cm. per atom of element for 0.025 e.v. ^a neutrons)			
Element	σ_{ac}	Period and Mass Number of Activity Formed	Element	σ_{ac}	Period and Mass Number of Activity Formed
A	0.61	110m A ⁴¹	Mg	0.088	10.2m Mg ²⁷
Ag	15.6; 46.6	2.3m Ag ¹⁰³ ; 22s Ag ¹¹⁰	Mn	13	2.59h Mn ⁵⁶
Al	0.21	2.4m Al ²⁸	Mo	0.095; 0.048	67h Mo ⁹⁹ ; 14m Mo ¹⁰¹
As	4.3	26.8h As ⁷⁶	N	2×10^{-4}	7.5s N ¹⁶
Au	96	2.7h Au ¹⁹⁸	Na	0.45	14.8h Na ²⁴
B	< 0.05	0.02s B ¹²	Nd	0.17	1.8h Nd ¹⁴⁹
Ba	0.37	85m Ba ¹³⁸	Ne	40s Ne ²³
B	0.01	2.9×10^6 y Be ¹⁰	Ni	0.03	2.6h Ni ⁶⁵
Bi	0.015	5.0d Bi ²¹⁰	O	4.4×10^{-7}	31s O ¹⁹
Br	1.4; 4.1; 1.1	4.4h Br ^{80m} ; 18m Br ⁸⁰ ; 34h Br ⁸²	Os	0.66; 2.2	31.9h Os ¹⁹¹ ; 17d Os ¹⁹³
C	0.001	5400y C ¹⁴	P	0.23	14.3d P ³²
Ca	0.001; 0.0004	30m Ca ⁴⁸ ; 2.5h Ca ⁴⁹	Pb	2.35×10^{-4}	3.3h Pb ²⁰⁹
Cd	1.2	6.6m Cd ¹¹³	Pd	2.9; 0.053	13h Pd ¹⁰⁹ ; 26m Pd ¹¹¹
Cd	0.25; 0.31; 0.1	48m Cd ¹¹¹ ; 2.3d Cd ¹¹⁵ ; 2.8h Cd ¹¹⁷	Pr	13	19.3h Pr ¹⁴²
Ce	0.12	33h Ce ¹⁴³	Pt	0.29; 1.2; 0.28	18h Pt ¹⁹⁷ ; 3.3d Pt ¹⁹⁷ ; 31m Pt ¹⁹⁹
Cl	0.14	37m Cl ³⁸	Rb	0.033	17.5m Rb ⁸⁸
Co	0.66	10.7m Co ⁶⁰	Re	38; 46	3.9d Re ¹⁸⁸ ; 18.9h Re ¹⁸⁸
Cr	0.49	26.5d Cr ⁵¹	Rh	137; 11.6	44s Rh ¹⁰⁴ ; 4.4m Rh ¹⁰⁴
Cs	3.0	3h Cs ¹³⁴	Ru	0.12	4.5h Ru ¹⁰⁵
Cu	1.9; 0.56	12.8h Cu ⁶⁴ ; 5m Cu ⁶⁶	S	2.2×10^{-3}	5m S ³⁷
Dy	716	2.5h Dy ¹⁶⁵	Sb	3.8	2.8d Sb ¹²²
Er	> 1.0	7.5h Er ¹⁷¹	Sc	22	85d Sc ⁴⁶
Eu	678	9.4h Eu ¹⁵²	Se	0.16; 0.23	59m Se ^{81m} ; 17m Se ⁸¹
F	0.01	12s F ²⁰	Si	0.0037	170m Si ³¹
Fe	0.001	46d Fe ⁶⁹	Sm	53; 1.4	47h Sm ¹⁵³ ; 21m Sm ¹⁵⁵
Ga	0.86; 1.3	20m Ga ⁷⁰ ; 14.1h Ga ⁷²	Sn	0.0039	9m Sn ¹²⁶
Gd	0.9	18h Gd ¹⁵⁹	Sr	0.13	2.7h Sr ⁸⁷
Ge	0.14; 0.005; 0.006	89m Ge ⁷⁸ ; 12h Ge ⁷⁷ ; 59s Ge ⁷⁷	Ta	0.034	16.2m Ta ¹⁸²
H	Very small	11y H ³	Tb	> 22	73.5d Tb ¹⁶⁰
He	Very small	Te	0.15; 0.041; 0.083	9.3h Te ¹²⁷ ; 72m Te ¹²⁹ ; 25m Te ¹³¹
Hf	3.5	46d Hf ¹⁸¹	Ti	0.0075	6m Ti ⁵¹
Hg	4.6; 0.023	64h Hg ¹⁹⁷ ; 5.5m Hg ²⁰⁵	Tl	0.078	4.2m Tl ²⁰⁶
Ho	49	27.3h Ho ¹⁶⁶	Tm	100	127d Tm ¹⁷⁰
I	7	25m I ¹²⁸	V	4.5	3.8m V ⁵²
In	138	54m In ¹¹⁶	W	9.9	24.1h W ¹⁸⁷
Ir	100; 79	1.5m Ir ¹⁹² ; 19h Ir ¹⁹⁴	Xe	0.021; 0.013	10m Xe ¹³⁵ ; 3.8m Xe ¹³⁷
K	0.066	12.4h K ⁴²	Y	1.2	61h Y ⁹⁰
Kr	0.055; 0.011	4.5h Kr ⁸⁶ ; 74m Kr ⁸⁷	Yb	14.8; 8.0	4.1d Yb ¹⁷⁵ ; 2.6h Yb ¹⁷⁷
La	8	40h La ¹⁴⁰	Zn	0.17	57m Zn ⁶⁹
Li	0.03	0.89s Li ⁸	Zr	9×10^{-3}	17h Zr ⁹⁷
Lu	19.5; 91	3.4h Lu ¹⁷⁶ ; 6.6d Lu ¹⁷⁷			

^a Data computed from values given in (40).

energies, provided charged particle products are not formed. The reaction probabilities should approach the geometric cross sections of the target nucleuses rather closely, and in general this is observed except for very low neutron energies where a remarkably strong interaction occurs. When neutrons move with velocities approximating those for thermal motion in the vicinity of room temperatures—i.e., ca. 0.025 e.v., the laws of quantum mechanics require that they behave as much larger bodies than when they move at high speed. The deBroglie relation between wave length and momentum may be utilized to estimate the cross section:

$$\sigma \leq \pi \lambda^2 = \pi (h/2\pi mv)^2 = \frac{h^2/4\pi m E}{E} = \frac{6.46 \times 10^{-19}}{E} \quad (8)$$

A simple computation thus reveals that the cross section for the capture of a thermal neutron may reach values as large as 10^{-18} sq. cm. per atom. Experimentally, however, the absorption cross sections for thermal neutrons are found to be somewhat smaller and to vary unpredictably from element to element, as well as from one isotope to another within an element, covering a range of values from 0.001 to $100,000 \times 10^{-24}$ sq. cm. per atom.

A summary of the known atomic cross sections for thermal neutrons is given in Table I, where the values listed have been expressed as square centimeters per atom of normal element. Magnitudes expressed in this fashion more truly reflect the differences in activation to be expected from one element to another than do the so-called isotopic cross sections used in physical considerations, for the reason that a correction for variations in the isotopic abundance ratios has been included. The atomic cross-section is thus equal to the product of the isotopic cross section and the fractional isotopic abundance. As is true for most nuclear constants, new and more accurate values of both isotopic cross sections and the relative isotopic abundances are appearing constantly. Slow neutron capture cross sections for many elements are now known to within $\approx 10\%$.

The variations of neutron cross sections with energy show several characteristics not exhibited in the nuclear reactions caused by energetic charged particles. Neutrons possessing energies in the thermal region exhibit capture cross sections which decrease with increasing energy according to the inverse square root of the latter quantity. At slightly higher energies (>1.0 e.v.) frequently resonance processes occur wherein the cross section may increase rapidly to a large peak value and then fall to its original relatively small value within an interval of only a few electron volts. At energies greater than 1000 e.v. (fast neutrons) the cross sections become and remain relatively constant at values approximating geometric cross sections. A cross section—energy plot illustrating a few of these points is given in Figure 2.

In conclusion, two generalizations derivable from the data of Table I should be noted because of their bearing on the use of thermal neutrons for activation analysis: Neutron activation analysis for the light elements ($Z < 10$) will not be possible owing to the extremely small absorption cross sections they show, and also because none other than short-lived radionuclides are formed; elements of odd atomic number may be detected with considerably greater sensitivity than those of even Z , both because of their intrinsically larger cross sections and because these elements are either monoisotopic or do not possess more than two stable isotopes.

The foregoing elementary discussion of nuclear cross sections has completed the background necessary to carry out an estimate of the order of magnitude of the flux of nuclear projectiles required if microgram amounts of elements are to be determined by means of activation analysis.

In forming this estimate, with the aid of Equation 5, it will be assumed that an activity of ten disintegrations per second is conveniently detectable with the requisite accuracy. The half-life of the radionuclides employed will be taken to be such that the irradiation time required for "half-saturation"—i.e., $S = 0.5$ —will be conveniently short. The mass of the element sought will be taken as 100. Finally, the atomic activation cross section will be taken as 5×10^{-26} sq. cm. per atom, a value believed to be fairly representative of the average over the periodic table as a whole. The numerical calculation shows then that a flux

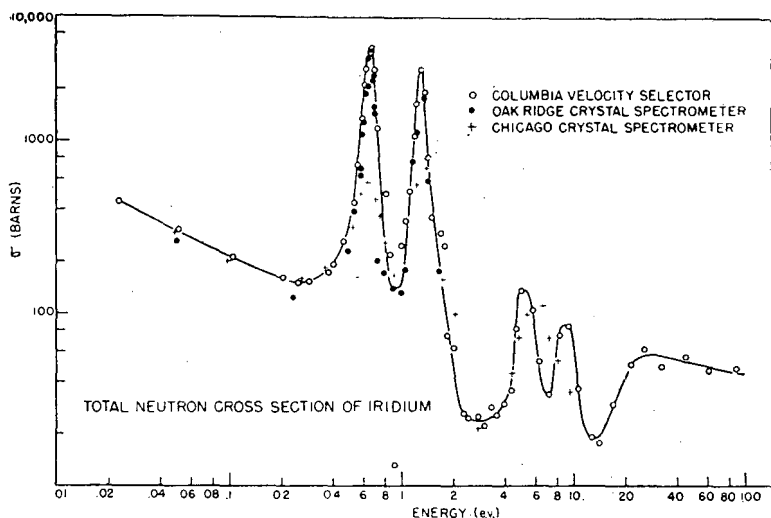


Figure 2. Variation of Total Neutron Cross Section with Energy from Natural Iridium

Log-log scales. Note resonance peaks. Data from Wollan and Shull (41)

of 6.6×10^{10} particles per sq. cm. per second will be required to detect 1 microgram of this hypothetical element with an error of $\approx 5\%$. A range of flux values between 5×10^{10} and 5×10^{12} particles per sq. cm. per second probably reflects the difference between the most and the least favorable combinations of cross section and half-life observed in practice.

The feasibility of the method of activation analysis clearly hinges upon the ease with which flux densities of 10^{10} to 10^{12} may be attained, so that the remainder of this section will be concerned with the present-day status and possibilities.

The cyclotron is assuredly the best known, and probably from the point of view of activation analysis, the most important source for energetic charged particles.

The flux of fast nucleons produced by this machine may be estimated by considering that a beam of 1 microampere of protons or deuterons corresponds to the flow of 6.3×10^{12} ions per second, and that beam currents of several hundreds of microamperes are not uncommon in present-day continuous wave machines. In a fairly typical irradiation where a 100- μ a. beam emerges from the cyclotron with approximately a 10 sq. cm. spread and then impinges upon a target, the nucleuses in this region are exposed to the relatively large flux of about 6×10^{13} particles per sq. cm. per second. The stopping of this number of 5 to 10 m.e.v. charged particles in a few millimeters of target material generates several kilowatts of energy which must be dissipated if serious losses of radioactivity due to volatilization are to be avoided.

When other than metallic samples are irradiated, forethought must be given to the possibility of this complication; some help may be gained from the recent study made at Columbia (27).

Exceptional sensitivities may be anticipated in activation analysis with the cyclotron. By way of illustration, a rough estimate will be made of the minimum concentration of sodium impurity detectable in a 1-sq. cm. thin aluminum sheet. The following conditions believed to be representative will be assumed:

The sample will be exposed to a 100- μ a. beam of 5 m.e.v. deuterons for exactly 12 minutes, after which a period of 30 minutes will be permitted to elapse in order that the strong 2.3-minute activity also produced in the aluminum by the reaction $Al^{27}(d, p)Al^{28}$ might decay to negligible proportions. Sodium will be assumed to be the only impurity in the aluminum, so that a chemical separation will not be required. The aluminum target may then be mounted, placed before a Geiger-Müller counter (or any other suitable detector) in a predetermined geometry, and counted. Suppose a counting rate of 100 counts per minute, or 1.67 counts per second, is observed which may be attributed to the 14.8-hour Na^{24} formed by the reaction, $Na^{23}(d, p)Na^{24}$ with the sodium impurity. This counting rate, corrected by means of Equation 4 for the 45-minute decay from the end of the

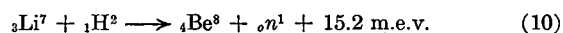
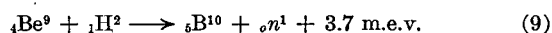
deuteron irradiation, becomes 1.73 counts per second. An estimate of the net counting yield will be required to compute the disintegration rate, A_t . Fortunately, the decay scheme for the disintegration of Na^{24} seems reasonably well established (39). Assuming the deuteron-irradiated aluminum foil was counted at 30% geometry, that $\epsilon = 1.0$ and $f_A = f_S = 1.0$ for the 1.39-m.e.v. β -particle, and that $\epsilon = 0.012$ and $\epsilon = 0.023$, again with $f_A = f_S = 1.0$, for the 1.38 and 2.76 m.e.v. γ -quanta emitted simultaneously, the net counting yield will be: $(1.0 \times 1.0 \times 0.3 \times 1.0 \times 1.0) + (1.0 \times 0.012 \times 0.3 \times 1.0 \times 1.0) + (1.0 \times 0.023 \times 0.3 \times 1.0 \times 1.0) = 0.31$. Hence, $A_t = 1.73/0.31 = 5.58$ disintegrations per second. Substituting this and the following into Equation 5: $M = 23$; $\theta = 1.00$; $f = 6 \times 10^{13}$; $\sigma_{ac} = 4.5 \times 10^{-25}$ (from Figure 1); $S = 9.3 \times 10^{-3}$, we have:

$$\begin{aligned} \text{Grams of sodium} &= \frac{5.58 \times 23}{6.02 \times 10^{23} \times 6 \times 10^{13} \times 4.5 \times 10^{-25} \times 9.3 \times 10^{-3} \times 1.00} \\ &= \frac{5.58 \times 23}{8.5 \times 10^{-10}} \end{aligned}$$

A concentration of about 0.1 p.p.m. sodium may be calculated then from the weight (6.8 mg.) of the assumed unit area of aluminum sheet one mil thick.

The foregoing estimate, because of a number of contributing uncertainties, is best regarded as reliable only in order of magnitude. The activation analysis was based upon the use of a very thin sheet of target material, so chosen that (f) would remain constant. Probably, in the actual employment of deuteron beams for analytical purposes, a sample of aluminum sufficiently thick to absorb the beam completely would be used. A distinctly lower specific activity would be produced under these circumstances, although the total activity would be at least an order of magnitude higher because of the more efficient use of the beam. Greater limiting sensitivities using thick targets might be expected, therefore, especially if chemical separations are performed. In actual analysis the comparative procedure, wherein the unknown and the known samples are irradiated together, would be employed. Calculations analogous to those just given may be desirable initially, however, in order to establish the range of sensitivity possible for a cyclotron beam with a known upper energy limit.

An alternative method for irradiation when using the cyclotron in activation analysis is to allow the primary beam of charged particles to strike a target, and thereby to produce a secondary flux of energetic neutrons. These fast neutrons may be employed then to effect the desired nuclear reaction, or they may be slowed down to thermal energies by some hydrogenous material, such as paraffin, placed as close as possible to the target, and then used. For the production of neutrons at the cyclotron, the lightest among the elements are chosen as targets because of the copious yields they give upon irradiation even with relatively low energy deuterons or protons. Two nuclear reactions which may be caused to proceed to yield an appreciable number of neutrons are:



The second of these two reactions is conducted whenever ultra-fast neutrons are requisite. Beryllium metal targets, by virtue of their low volatility and comparatively good heat transfer characteristics, are generally preferred for the production of cyclotron-sustained thermal neutron sources. Good source intensities may be created, as is attested by the recent report that as many as $3.7 \pm 0.4 \times 10^{10}$ neutrons per second per $\mu\text{a.}$ are produced with 10-m.e.v. deuterons on beryllium (36). This neutron intensity is not so great, however, as that of the beam of charged particles in the cyclotron. Since 1 $\mu\text{a.}$ corresponds to 6.3×10^{12} particles per second, it is seen that only one fast neutron is formed per 170 primary energetic deuterons. There is a second equally important factor to be considered in this comparison. The colimated nature of the flow of charged particles accelerated in the cyclotron, and the small cross-sectional area of the beam together make for very high bombardment geometries in the production of artificial radioactivity. Effectively, all the fast charged particles

emitted by the cyclotron can be subtended by a few square centimeters of target. On the other hand, the deuteron-irradiated beryllium target in the cyclotron emits neutrons in all directions with roughly equal probability. Elementary geometric reflections will show that only a fraction of the total of these fast neutrons will be intercepted by a unit area of target:

Consider a point source of neutrons to be generated when a 100- $\mu\text{a.}$ beam of 10-m.e.v. deuterons falls upon the face of a block of beryllium metal 2 cm. thick; then, 3.7×10^{12} neutrons per second will be radiated over a solid angle of 360° . If a 1-sq. cm. disk of material to be activated is placed against the rear face of this target it will intercept approximately 2% of the fast neutrons, or it will be exposed to a flux of about 7.4×10^{11} neutrons per sq. cm. per second. Fast neutron cross sections larger by a factor of 10^3 to 10^4 will be required, therefore, if quantities of radioactivity comparable with those formed by the same deuteron beam acting directly upon the target are to be produced.

The order of magnitude of cyclotron-maintained thermal neutron fluxes will be of relevance to this discussion of the potentialities of the method of activation analysis, because the cross sections for slow neutron capture reactions have been shown to exceed those for energetic charged particles. Usually, slow neutron sources of this type are formed by the slowing down of fast neutrons with thick layers of paraffin placed as close as possible to a beryllium target and surrounding it on three sides. The slowing down process, or moderation, requires an average of 20 to 30 collisions between a given neutron and the hydrogen atoms of the paraffin. A fairly complete "thermalization" thus occurs within about 3 cm. from the source of the primary fast neutrons. These thermal neutrons subsequently diffuse outward through the paraffin in a manner analogous to a gas at room temperature and at low pressure until they are captured by impurities or by hydrogen (parasitic losses) or else escape from the boundary (leakage losses). An enclosing layer of thin cadmium sheet is placed at this boundary to prevent the leakage of neutrons into the room. Furthermore, because energetic γ -radiations also are given out by the target, the paraffin block is shielded on its periphery by several inches of lead.

The slow neutron flux passing through a thin foil of unit area placed in the paraffin at a distance of 5 cm. from a cyclotron source of 3.7×10^{12} neutrons per second may be estimated approximately by computing the geometry for this distance, and assuming the flux moderated neutrons to be roughly the same as the flux of fast neutrons at the same point in the absence of the paraffin. Thus, an aluminum metal foil placed at the above-mentioned distance would be exposed to a slow flux of about 10^{10} neutrons per sq. cm. per second. In principle, an activation analysis for sodium impurity in this foil might be conducted using the neutron capture reaction: $\text{Na}^{23}(n, \gamma)\text{Na}^{24}$ to give the characteristic 14.8 hour Na^{24} . Much lower limiting sensitivities would be attainable in this case, however, than with a direct irradiation of the sample by 10-m.e.v. deuterons, provided an otherwise identical procedure is followed. The activation cross section of sodium for the capture of slow neutrons is 4.5×10^{-25} sq. cm. per atom, whereas with energetic deuterons the activation occurs with almost the same cross section but with a flux 6300 times greater. By reason of this advantage factor, unless the element to be determined by activation possesses a neutron capture cross section at least one thousand times greater than that for the charged particle reaction, a direct cyclotron bombardment may be preferable. Neutron reactions with the heavier elements will be favored, however, owing to the increasingly higher threshold energies required to effect charged particle reactions as the atomic number increases. Furthermore, because negligible amounts of heat are evolved and recoil effects are rarely important, slow neutron capture reactions may take precedence in specific instances.

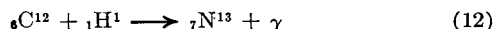
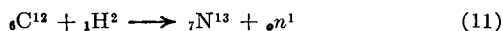
Low deuteron energies may be employed in the activation of the light elements, thereby making the use of less expensive machines of simpler design, such as electrostatic generators, feasible.

Table II. Determination of Carbon in Iron by Activation Analysis (3)

AFe	$C^{12}(d, n) 9.93m N^{13}$			% C, Chemical Analysis	$C^{12}(p\gamma) 9.93m N^{13}$			
	ASiC	AFe:ASiC	% C		% C	AFe:ASiC	ASiC	AFe
510	21000	0.024	0.06 ± 0.02	0.03
490	22000	0.022	0.06 ± 0.02					
700	20500	0.022	0.06 ± 0.01	0.05	0.04 ± 0.04	0.016	2670	42
500	26500	0.019	0.05 ± 0.01					
1000	21500	0.047	0.13 ± 0.01	0.12	0.11 ± 0.02	0.028	4500	125
545	11800	0.046	0.13 ± 0.01		0.12 ± 0.02	0.031	6000	188
850	12500	0.068	0.19 ± 0.02	0.14	0.13 ± 0.02	0.033	8200	273
960	14600	0.066	0.18 ± 0.02		0.14 ± 0.02	0.036	5600	200
11000	32200	0.344	0.95 ± 0.01	1.00	0.99 ± 0.03	0.256	5700	1460
890	2650	0.336	0.94 ± 0.02		1.00 ± 0.04	0.261	2300	600

One-minute irradiation of $30 \times 30 \times 0.2$ mm. sample together with a 1.12 sq. cm. silicon carbide monitor containing 30% carbon by a 20 μ a. beam of 800 k.e.v. deuterons. (10-minute irradiations with protons.)

A useful illustrative example of the employment of a low voltage nuclear accelerator for the rapid, accurate analysis of small amounts of carbon in iron may be taken from a recent publication (3). The samples to be analyzed were irradiated for 10 minutes with a 20- μ a. beam of either 0.8-m.e.v. deuterons or protons to give the following nuclear reactions:



The sample of unknown carbon content and an analyzed silicon carbide monitor (ca. 30% carbon) were fastened to a circular disk which could be rotated through the deuteron or proton beam, thereby irradiating each alternately so as to minimize unavoidable fluctuations in the operation of the accelerator. The measured activity of the 9.93-minute N^{13} produced in both the unknown and the monitor were compared, and the carbon content of the former sample was computed using Equation 7. A collation of the results from the nuclear chemical method with the values obtained by means of a conventional chemical analysis on the identical samples, shown in Table II, appears to demonstrate that in its present state of refinement the activation method will yield reliable analyses on metal samples containing as little as 0.05% carbon.

Inherently, the method of activation analysis should be more sensitive by at least an order of magnitude, as may be shown by a simple numerical estimate using Equation 5.

In this instance, the calculation will be made assuming that the N^{13} positron activity is determined within 5 minutes after bombardment, and that the minimum acceptable counting rate is set at 1000 counts per minute, or 16.7 counts per second. Correction of this latter quantity for decay before the radioassay using a 9.93-minute half-life gives 23.7 counts per second. An estimate of the net counting yield, made on the basis of the known decay scheme (39), assuming 30% counting geometry with a Geiger-Müller tube, gives: $(1.0 \times 1.0 \times 0.3 \times 1.0 \times 1.0) + (2.0 \times 0.0032 \times 0.3 \times 1.0 \times 1.0) = 0.32$. Reference to the published excitation curve for the reaction $C^{12}(d, n)N^{13}$ (25) indicates that an average cross section of about 10^{-27} sq. cm. per atom will be effective at 700 k.e.v. Accordingly,

Grams of carbon =

$$\frac{12 \times 23.7/0.32}{6.02 \times 10^{23} \times 1.2 \times 10^{13} \times 10^{-27} \times 0.5 \times 1.0} = 2 \times 10^{-7}$$

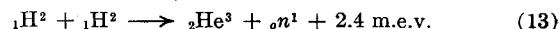
Indication of the enormous intrinsic sensitivity of this approach to carbon analysis may be found in the great care taken in the work cited to clean the metal surfaces of grease, and henceforth, until the bombardment, to avoid contamination. Because the depth of penetration of the relatively low energy deuterons or protons employed into the iron was of the order of only 1.5 to 2.0 microns, even a monolayer of grease would be enough to simulate a carbon content of a few hundredths of 1%. Actually in this study the most serious carbon contamination resulted from the oil vapor present in the vacuum irradiation chamber. An attempt to eliminate this interference by covering the samples with thin alu-

minum foils met with only partial success, owing to the penetration of these coverings by recoil carbon molecule ions produced in the deuteron beam. Recoil effects and volatilization losses in the target chamber are the cause of annoyance and sometimes great uncertainties at higher energies, as Seaborg (31) has pointed out in connection with cyclotron studies

Least the stress on the necessity for large fluxes lead to the impression that this is the only factor determining sensitivity in activation analysis, it should be added that some high energy nuclear machines such as betatrons and synchro-

trons which are capable of producing large fluxes of fast electrons or penetrating γ -quanta compare unfavorably with cyclotrons and modern day thermal neutron sources for the quantitative production of radioactivity. This situation derives from the fact that the nuclear reaction probabilities for electro- and photodisintegration processes are thousands of times smaller than those for protons, deuterons, α -particles, or neutrons.

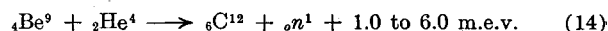
The low voltage neutron generator must be regarded as an important development in the direction of the manufacture of nuclear machines of comparatively modest cost for the production of radioactivity. Here the nuclear reaction is:



in which a target made from heavy water ice (or deuterated paraffin) is bombarded with 200-k.e.v. deuterons. A copious emission of neutrons results when deuteron beam currents of several hundred microamperes are used. One such apparatus recently constructed at the Institute of Physical Chemistry of the University of Uppsala (38) has been reported to give intensities as large as 8×10^7 neutrons per second, a magnitude roughly equivalent to the number of neutrons emitted by a 10-gram radium-beryllium mixture. Manifestly, this type of apparatus will have value for the laboratory preparation of radioactive tracers; if it could be developed to the point where intensities of an order of magnitude greater might be achieved, it would almost certainly become an important tool for activation analysis.

As the radium-beryllium neutron source has been mentioned, for the sake of completeness it will be considered briefly, for although the intensities produced are relatively low, it may prove useful on occasion, as in the activation analysis for certain rare earths in naturally occurring mixtures, or for several of the noble metals in platinum ores.

The production of primary fast neutrons in this case results from the bombardment of the beryllium by the energetic α -particles emitted in the decay of the radium and its daughter radioactivities according to:



The number-energy spectrum of the fast neutrons is complex, because there are several excited levels in the compound nucleus, C^{13} , each corresponding to a different reaction energy, and there are several α -particles each of differing energy from the equilibrium mixture of the radium plus its active decay products. The intensity of neutrons from a radium-beryllium source is proportional to the mass of radium for a given amount of beryllium; alternatively, for a given amount of radium the source strength increases with mass of beryllium in such a way that a large proportion of the latter is desirable. Because, however, the volume of the source tends to become large a compromise ratio is employed; values of the beryllium-radium mass ratio between 3 and 10 find the most frequent use. The neutron intensity to be

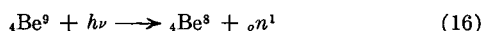
expected from a pressed radium-beryllium mixture of known composition may be estimated approximately by the following relation (1):

$$\text{Neutrons per second} \approx 1.3 \times 10^7 \frac{M_{\text{Ra}} M_{\text{Be}}}{M_{\text{Ra}} + M_{\text{Be}}} \quad (15)$$

where M_{Ra} , M_{Be} are the masses, in grams, of radium and beryllium, respectively. Recently published measurements (34) of the intensity of a source containing 500 mg. of radium (as radium bromide) mixed with 3000 mg. of beryllium metal powder gave a value of $5.5 \pm 0.4 \times 10^6$ neutrons per second in good agreement with Equation 15.

The concurrence of an appreciable number of high energy γ -rays together with the α -emission from radium sources introduces a considerable inconvenience in the handling of neutron sources of this type. The naturally occurring radioactive isotope of the element polonium, which emits α -rays and only very little quantum radiation, may be used to good advantage therefore when γ -radiations must be absent. Unfortunately, owing to the 140-day half-life of Po^{210} , the intensities of neutron sources made with this ingredient show a fairly pronounced diminution with time.

The production of neutron sources sustained by artificial radioactive elements appears to offer some possibilities for future development. Perhaps the most promising among these is the photodisintegration to yield neutrons which takes place when beryllium is exposed to γ -radiation of greater than 1.63-m.e.v. energy:



Suitable radionuclides are limited therefore to those which emit γ -quanta exceeding the 1.6-m.e.v. threshold preferably in large abundance. Ideally, the half-life of the isotope should be long. Furthermore, in order that intensely active preparations may be made, as, for example, by irradiation in the chain-reacting pile, the cross section for neutron capture must be appreciable. Measurements of the yields (28) from photoneutron sources maintained by pile-produced radionuclides suggest that the 60-day Sb^{124} might prove useful in this capacity. The observed yield of 3.2×10^6 neutrons per second per curie compares very well with that obtained from conventional radium-beryllium sources. Also, the volume of the antimony-beryllium source compares favorably; a disadvantage is that the source decays with a 2 months' half-time. The primary neutrons emitted by the antimony-beryllium source are monokinetic and possess an energy of 24 k.e.v.

The simplicity of the construction and use of radium-beryllium or antimony-beryllium neutron sources is such that their potentialities for radioactivity studies deserve a much more widespread recognition among chemists than at present. In certain instances where conventional analytical procedures require difficult chemical separations, as with rare earth mixtures, a direct activation analysis using a "natural" source of neutrons may be feasible. Thus, amounts of dysprosium occurring in concentrations down to 0.01% in a 1-gram sample of yttrium may be estimated by activation with neutrons from a 600-mg. radium-beryllium source. The employment of the antimony-beryllium neutron source, placed at the center of a simple paraffin geometry, may be practical for many metallurgical analyses where alloy constituents rarely have to be determined in concentrations below $10^{-3}\%$. In dealing with the precious metals, for example, a calculation shows that less than 0.1% of rhodium and 0.01% of iridium alloyed with platinum may be detected.

The possibility for using curie-strength natural or photoneutron sources to analyze for elements which strongly absorb thermal neutrons, but which are not made radioactive for one reason or another, deserves to be mentioned. In this variation of the method of activation analysis, the unknown sample is placed be-

tween the source of slow neutrons and a thin indium or rhodium metal foil. A comparison is then made between the activation of the indium with the unknown, and then with a reference substituted in the identical position. Recently, Martelly and Süe (24) have described the application of this method to the determination of as little as 0.1% boron in silica with an absolute precision of 0.015%.

ACTIVATION ANALYSIS WITH THE CHAIN-REACTING PILE

The chain-reacting pile is without a peer as a tool for the general quantitative production of radioactivity by reason of the magnitude and spacial extent of the thermal neutron flux it is able to sustain. The pile, as a source of neutrons, excels the cyclotron in respect to both intensity and the magnitude of the effective flux produced. This statement may be illustrated by several typical figures which hold for the graphite-natural uranium reactor in operation at the Oak Ridge National Laboratory. Here, the maximum thermal flux is between 1 and 2×10^{12} neutrons per sq. cm. per second. Experimental samples may be inserted into the pile at several points for irradiation, one of the most frequently used facilities being a pneumatic transfer tube which is employed for short irradiations of fractional gram quantities at 57% of the maximum flux. Larger samples to be exposed for periods extending from several days up to many months are placed in sealed aluminum cans which fit into holes drilled perpendicularly to the axis of long graphite bars, square in cross section, known as "stringers" which may be inserted into the pile. The flux acting upon a sample placed in a stringer may vary between 25 and 35% of the maximum, depending upon its position. The bombardment geometry is 100%, because the target is placed inside the pile.

A straightforward numerical calculation using Equation 5 and the activation cross sections listed in Table I will show that, except for the light elements, enormous sensitivities can be obtained by irradiation with thermal neutron fluxes ranging from 2.5 to 5.7×10^{11} neutrons per sq. cm. per second. As has been pointed out (42), it is possible for individuals, through the Atomic Energy Commission isotope distribution program, to obtain service irradiations in the Oak Ridge pile. Accordingly, a few illustrative examples of the use of the pile will be given, as it may be feasible, apart from limitations imposed by the half-life, to conduct activation analyses of special materials by means of this facility.

The most rudimentary type of analysis that may be carried out with the pile is simply to irradiate the unknown sample for a few minutes, and then determine the decay of the mixture of activities produced. A resolution of the decay curve is performed then by the method of successive differences—i.e., curve "peeling-off"—in an attempt to find the half-lives of the components. Subsequently, the qualitative analysis is completed by assigning the observed decay periods to the appropriate elements with the assistance of a compilation of nuclear data, if necessary. An illustration of this procedure may be found in Figure 3, where the decay curve has been plotted for a pile-irradiated sample of pure rubidium carbonate. The unmistakable presence of small amounts of potassium and cesium is indicated. Sometimes the identities of the half-lives formed in the unknown are not recognized immediately. Help may be obtained then by reference to the particularly useful table of Clark and Jones (10) wherein a listing according to the magnitude of the decay time has been given.

There are several limitations to this simple procedure for the qualitative analysis of unknowns, however. First, the method may prove time-consuming, because occasionally it is necessary to measure the decay of the gross activity over a long period to determine the exact contribution from the component of greatest half-life. Furthermore, in general the analysis of a decay curve possessing more than three components yields unreliable short

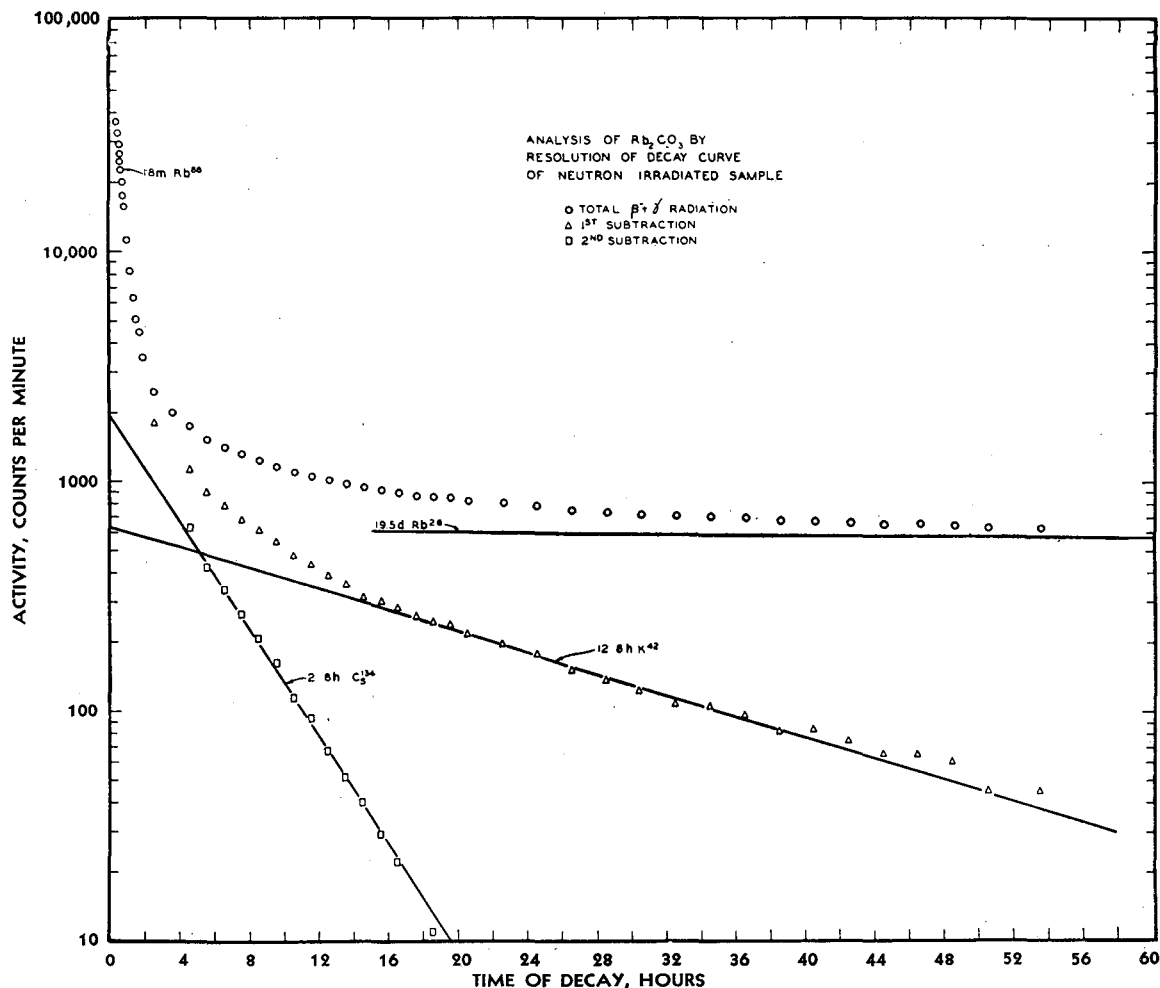


Figure 3. Qualitative Analysis by Means of Activation

Decay curve taken on pile neutron-irradiated rubidium carbonate

half-lives because of the accumulation of large errors from the previous successive subtractions. In certain cases, as for example, in the attempt to find small amounts of molybdenum in rhenium, yttrium in dysprosium, or copper in gold, the activation of the major constituent may be so great that the decay of the activity from the minor constituent cannot be determined unless chemical separations are performed. Finally, if the half-lives of two radionuclides do not differ by more than about 50% from each other, the composite decay curve cannot be resolved accurately, if at all.

Sometimes quantitative activation analyses of binary or ternary mixtures can be accomplished by the use of techniques based on the differences in the radiations emitted by the radionuclides formed. The analyses of mixtures of sodium and potassium carbonate may serve to illustrate one such procedure.

In this case, the 14.8-hour Na^{24} and the 12.4-hour K^{42} produced by neutron activation possess half-lives too nearly the same to permit a resolution of the composite gross decay curve they would yield if the total β -radiations were counted. However, the β -ray emitted in the decay of the sodium activity possesses a maximum energy of 1.39 m.e.v. compared with the potassium activity where β -particles of a maximum energy of 3.58 m.e.v. are radiated. As may be seen from Figure 4, the less energetic sodium β -radiations ($\text{Na}\beta$) will be completely absorbed by a thickness of aluminum of 700 mg. per sq. cm. surface density, whereas the potassium β -radiations ($\text{K}\beta$) will not disappear until 1700 mg. per sq. cm. of aluminum have been interposed between the sample and the Geiger-Müller counter. The energetic γ -rays emitted by the radiosodium and potassium will be absorbed only very slightly by these thicknesses of aluminum. If

the symbols, A_{700} and A_{1700} , designate the total counting rates observed with 700 and 1700 mg. of aluminum per sq. cm. absorber in position, respectively, and if $\text{K}\beta$, $\text{K}\gamma$, and $\text{Na}\gamma$ represent the contributions to these counting rates from the β -, γ -, and γ -radiations emitted by potassium and sodium, respectively, the following relations will hold:

$$A_{700} = \text{K}\beta + \text{K}\gamma + \text{Na}\gamma \quad (17)$$

$$A_{1700} = \text{K}\gamma + \text{Na}\gamma \quad (18)$$

Equations 17 and 18 may be subtracted to find $\text{K}\beta$ after correcting for the slightly greater absorption of the γ -radiations of Na^{24} and K^{42} in going from 700 to 1700 mg. of aluminum per sq. cm.

Next, the ratio, R , of the counting rates, $\text{K}\gamma$ to $\text{K}\beta$, is determined at 700 mg. per sq. cm. using a sample of pure 12.4-hour K^{42} activity, so that:

$$\text{K}\beta = A_{700} - 1.024A_{1700} \quad (19)$$

$$\text{K}\gamma = R\text{K}\beta = R(A_{700} - 1.02A_{1700}) \quad (20)$$

$$\text{Na}\gamma = A_{1700} - R(A_{700} - 1.02A_{1700}) \quad (21)$$

Table III. Analysis of Sodium-Potassium Mixtures after Neutron Activation Using the Technique of Differential Absorption

Sample No.	% Na from Gravimetric Data	% Na Found by Activation Analysis
1	19.4	21.0
2	33.3	35.4
3	58.3	58.2
4	83.3	81.5
5	97.2	94.2

or,

$$Na\gamma:K\gamma = \frac{A_{1700}}{R(A_{700} - 1.02A_{1700})} - 1 \quad (22)$$

The composition by weight of sodium and potassium atoms in a given mixture may be determined from the experimentally determined γ count ratio, corrected for decay from the end of bombardment, if the following information is available: the number of γ -rays per disintegration; the counting efficiency, ϵ , per γ -ray; and the ratio of the activation cross sections for slow neutrons.

A few typical observations made during a rapid preliminary study of this method of differential absorption using the pile for the activations may be given by way of illustration.

Five 100-mg. mixtures of analytical reagent grade sodium and potassium carbonate of known composition were sealed each in a quartz tube 3 cm. long 4 mm. in inside diameter, and then all were placed in a plastic "rabbit" and irradiated at the end of the pneumatic tube for exactly 5 minutes. Each sample was dissolved in distilled water and made up to 5-ml. total volume in small glass-stoppered volumetric flasks. Aliquots ranging from 100 to 500 λ were withdrawn by means of micropipets and evaporated in the center of 2.5-cm. (1-inch) diameter watch glasses, which in turn were attached to the center of 2.5 \times 3.25 inch thin

aluminum cards in order that the radioassay might be performed at a definite geometry. The value of R was determined at the same time and under the same conditions as the measurements on the unknowns, and was found to be 0.0277. The fraction of sodium in a given mixture was estimated from the equation:

$$\% Na = \frac{3.75 \times 10^{-2}(Na\gamma/K\gamma)_o}{1 + 3.75 \times 10^{-2}(Na\gamma/K\gamma)_o} \times 100 \quad (23)$$

A comparison of the observed compositions with those estimated from the gravimetric measurements conducted during the preparation of the mixtures is given in Table III.

This procedure clearly possesses the virtues of simplicity and speed; however, a number of limitations are also evident: Apart from the necessity of measuring the ratio, $K\gamma$ to $K\beta$ under exactly the same conditions as with the unknown sample, an inspection of Equation 22 will show that sometimes, owing to the relatively small difference in counting rates under 700 and 1800 mg. per sq. cm. absorber, respectively, that may be observed, small errors in the individual activity measurements will lead to large errors in the net result. The method may be invalidated if other radioactive impurities be present, particularly if they radiate energetic β -particles. In this case, chemical separations will be required, and the chief advantage of the differential absorption technique over the comparative procedure in activation analysis will be lost.

As a final example of the use of the pile in activation analysis, the employment of the absolute method in the determination of the amount of manganese in 3S aluminum is described.

A preliminary 5-minute irradiation of a small, carefully cleaned and weighed piece of the aluminum sheet was conducted, and the composite decay curve shown in Figure 5 was recorded. The resolution of the curve indicated the presence of small amounts of sodium impurities, activated by the reaction $Na^{23}(n, \gamma) 14.8$ -hour Na^{24} , in addition to strong 2.3-minute Al^{28} and 2.59-hour Mn^{56} activities. There was no evidence of competing reactions

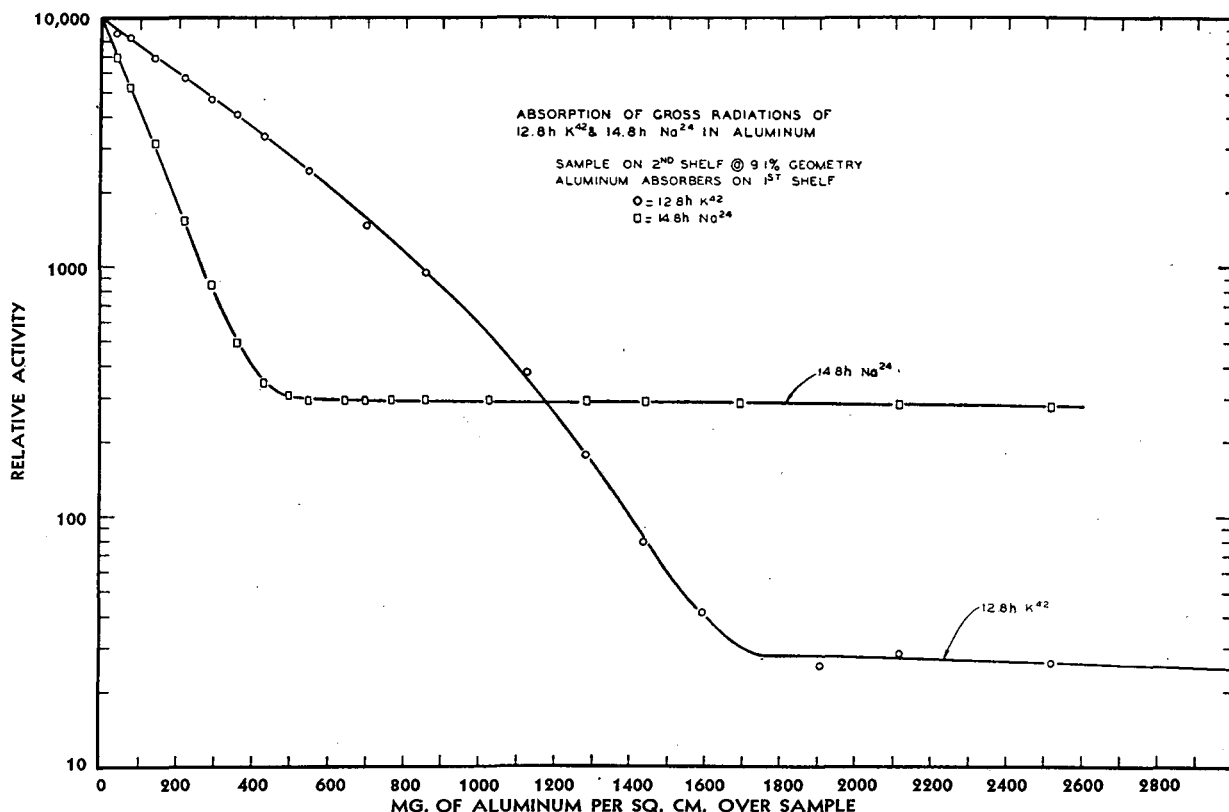


Figure 4. Aluminum Absorption Curves

Experimental basis for application of technique of differential absorption in analysis of mixtures of sodium and potassium carbonates

of the type, $\text{Al}^{27}(n, p)$ 10.2-minute Mg^{27} and $\text{Al}^{27}(n, \alpha)$ 14.8-hour Na^{24} , even though roughly 5% of the neutrons at the pneumatic tube terminal possess energies extending above the cadmium cut-off (0.18 e.v.) to as high as several million electron volts. The extrapolated activity of the 2.6-hour Mn^{56} (Figure 5) together with relevant bombardment and counting data was used to estimate that the manganese-aluminum alloy contained about 1% manganese.

A second pile irradiation of another alloy sample was conducted to determine the manganese content more exactly. In this experiment, a flux monitor was exposed together with a cleaned, 25-mg. sample for exactly 5 minutes. An assay of the monitor using a calibrated ion chamber (17) made possible an accurate determination of the thermal flux during the irradiation. This was 6.4×10^{11} neutrons per sq. cm. per second. A 30-minute lapse was taken to allow for the disappearance of the strong activity produced in the aluminum. The alloy was dissolved and the manganese activity was separated chemically with the aid of 1 mg. of manganese carrier. The procedure followed paralleled that described by Clark and Overman (11). The final manganese-containing precipitate was dissolved in 2 drops of concentrated hydrochloric acid and transferred quantitatively to a mount using micropipet.

The mount for the radioactivity quantification was a 1-mil polystyrene film (2.6 mg. per sq. cm.) upon which the sample was evaporated to dryness slowly under an infrared lamp. Just before completion of the evaporation a drop of ammonium hydroxide was added to the sample in order to convert the deliquescent manganese chloride to the hydrous oxide. The polystyrene film was mounted over a 1-inch diameter hole in a standard aluminum card, using polystyrene cement and taking care that the precipitate was centered accurately. The sample was then covered with a second 1-mil polystyrene sheet to prevent contamination of the counting geometry in case of an accidental spill.

The complete assembly holding the sample thus prepared was counted in an accurately predetermined counting position (2.95% geometry) with a 3.0 mg. per sq. cm. mica end-window Geiger-Müller tube for a period sufficiently long to give a 2% statistical uncertainty in the counting rate. The net observed rate corrected for counting loss, background, and counts due to γ -rays, was 8420 counts per minute which, corrected for 88% chemical yield, becomes 9570 counts per minute, or 159.5 counts per second. The net counting yield for the β -decay rate was estimated using the known disintegration scheme for Mn^{56} (13, 35) together with previously estimated values for the absorption and scattering factors, f_A and f_S , as follows: $Y_{\text{net}} = (0.60 \times 0.0295 \times 0.96 \times 1.04) + (0.25 \times 0.0295 \times 0.77 \times 1.05) + (0.15 \times$

$0.0295 \times 0.69 \times 1.07) = 0.0270$. The percentage of manganese may then be computed by substitution in the formula:

$$\% \text{ manganese} = \frac{(C\beta/Y_{\text{net}}) \times M}{6.02 \times 10^{23} \times \text{grams of alloy} \times nv\sigma_{\text{ac}}(1 - e^{-\lambda t})} \times 100 \quad (24)$$

One further point with respect to the proper use of the activation cross section, σ_{ac} , taken from Table I, must be made before the numerical calculation indicated can be completed. The value of 13×10^{-24} sq. cm. per atom listed above holds only for the particular neutron velocity, $v_0 = 2200$ meters per second, corresponding to a neutron energy of 0.025 e.v. Pile neutrons, however, are present in a somewhat different number-energy spectrum. In the first place, about 5% of the activations produced in manganese irradiated at the pneumatic tube terminal result from the capture of fast neutrons, as may be shown by a comparison of the radioactivities formed in identical samples, one exposed unshielded and the other wrapped in 40-mil cadmium foil. Accordingly, the observed net counting rate above must be multiplied by 0.95 to give the activation produced by neutrons whose cross sections obey the $1/v$ law. Secondly, although the thermal part of the pile neutron spectrum exhibits a Maxwellian velocity distribution, the average velocity is somewhat in excess of 2200 meters per second (300° K.). The standard value of σ_{ac} for Mn^{56} , therefore, must be increased proportionately. In general, to find the average cross section, $\bar{\sigma}$, of a $1/v$ absorber in any Maxwellian distribution, the value given in Table I should be multiplied by $\frac{1}{1.128} \sqrt{\frac{300}{T}}$. For the case in hand $\bar{\sigma}_{\text{ac}} = 0.658\sigma_{\text{ac}} = 8.5 \times 10^{-24}$.

$$\% \text{ manganese} = \frac{(159.5/2.7 \times 10^{-2}) \times 55}{6.02 \times 10^{23} \times 2.5 \times 10^{-2} \times 6.4 \times 10^{11} \times 8.5 \times 10^{-24} \times 2.22 \times 10^{-3}} \times 100 = 1.69$$

A chemical analysis of this same alloy gave a manganese content of 1.48%. The agreement between the two values is within the error of the former, almost certainly, in the light of the numerous uncertainties and known experimental errors in the absolute procedure. A much more accurate analysis for manganese would be obtained using the comparative method.

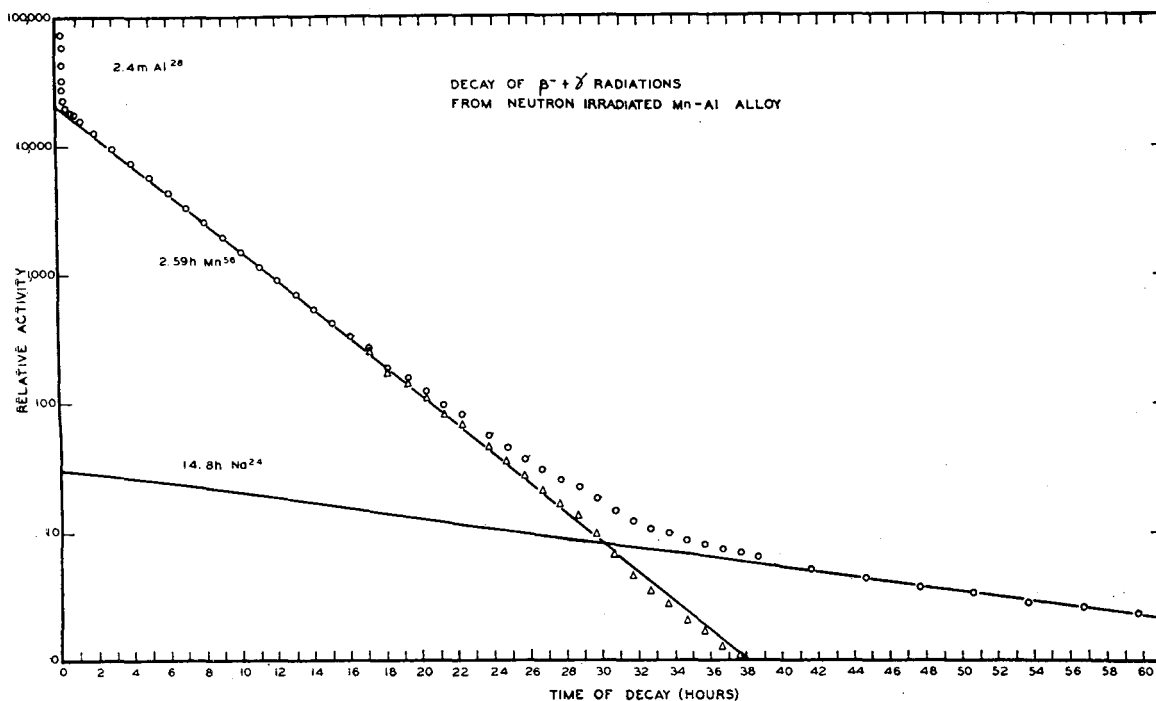


Figure 5. Analysis of Manganese-Aluminum Alloy by Radioactivation
Decay curve for pile neutron-irradiated 3S aluminum

The method of activation analysis may be employed to determine the isotopic abundance ratios of stable isotopes when these give acceptable periods. Again, using the comparative method, changes in the abundance ratio may be measured with a precision rivaling that of modern mass spectrometry. Already this method has been employed to test the separation of the chlorine isotopes in a thermal diffusion tower (18). The following example, taken from preliminary observations made in 1946 at the Oak Ridge National Laboratory by J. A. Swartout (?) will serve as an illustration:

The isotopic composition of a preparation of the copper isotopes produced by the calutron was determined. Mass spectrographic analyses conducted by the Y-12 laboratory under the supervision of A. E. Cameron had indicated $97 \pm 1\%$ of mass 63 and $3 \pm 1\%$ of mass 65 in the sample of copper received. A quantity of this preparation weighing 0.026 mg. was placed in the pile and irradiated for 5 minutes to form the 12.8-hour Cu^{64} and the 5-minute Cu^{66} activities. The decay of this mixed activity was followed to make possible an accurate resolution of the curve into its two components. Extrapolating to zero time, 4×10^4 β -counts per minute could be attributed to the 5-minute period when the sample was measured at 30% geometry. Using this information, together with the flux of neutrons and the isotopic cross section for Cu^{65} , a calculated value of 9.3×10^{-7} gram of mass 65 was estimated to be present in the sample. Thus, a value of 3.5% Cu^{65} was deduced, which is in better agreement with the mass spectrographic analysis than would be expected, owing to the numerous approximations and errors in the activation procedure.

CONCLUSIONS

The object of the foregoing discussion has been to summarize the present-day status of the method of activation analysis and to illustrate its application by reference and by example. The procedure, as an analytical technique, is assuredly in its infancy although the necessary physical foundations for its establishment as a method of wide generality are being completed rapidly. Thus far, the most frequent application of the technique has been in the analysis of metals and alloys. In practice, the feasibility of the application of the method to a given analytical problem must be determined by a prior consideration of the facts of nuclear phenomena. The means for nuclear excitation, the kind of instrumentation best suited for radioactivity detection, and the necessity for chemical separations are factors of especial importance. Because short-lived induced activities usually give the largest sensitivities, and because chemical separations are desirable in general, the success of the method in the future may depend upon the evolution of rapid specific isolation procedures. The need for such chemical separations, indeed, is responsible for one of the standing problems in fission product radiochemistry. In the experience of the author, separations based on differences in volatility or in solvent extraction may be performed rapidly and efficiently on occasion.

The extent of the application of the method of activation as a procedure for the estimation of microconstituents outside of atomic energy establishments would seem to depend in an important way upon the future availability of nuclear production apparatus at modest cost. Ideally, an artificial source capable of setting up a neutron flux of 10^{10} neutrons per sq. cm. per second would appear desirable. A source intensity of a magnitude roughly 50 times greater would be required because of the poor irradiation geometries attainable. Either a low voltage type linear accelerator or a small, compactly designed cyclotron might be developed to meet these specifications, provided beam currents of the order of 1 milliammeter (1000 μa .) could be created. Such a machine could then be used for charged particle bombardment of the light elements or for the production of fast and slow neutrons.

Finally, the possibility of continuous instrumental analysis may be mentioned. If samples could be arranged to pass, as on a moving belt, successively under a source and then under a

detector, a neat procedure for industrial control might become feasible.

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Instruments for Measuring Radioactivity

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One of the most widely used instruments in radioactive tracer studies is the Geiger-Müller counter, which has attained this widespread use primarily because of its simplicity, sensitivity, and availability. Less familiar is the use of proportional counters for the detection of weakly ionizing radiations. Beta-proportional counters of the flow type which have counting yields over 50% and which are especially useful for low energy β - and x-ray emitters are described. Permanently filled β -proportional

counters have shown no change of characteristics after 10^{14} counts. Because of the simplicity of sample preparation many tracer experiments can be so designed that the use of a γ -emitting isotope in conjunction with the high pressure γ -chamber will in some cases yield results in one tenth the time and effort that would otherwise be required if a β -emitter were used. Ionization chambers for C^{14} measurements are especially useful for the assay of samples of low specific activity.

MEASUREMENT of radioactivity is generally based on the detection of ionization produced in gases by energetic charged particles. The charged particles may be of nuclear origin—e.g., β -particles, positrons, α -particles—or they may be electrons produced by the interaction of γ - or x-rays with matter.

The density of ionization along the path of a charged particle is dependent on its velocity, charge, and the nature and pressure of the gas in the detector. A 0.5-m.e.v. β -particle has a range of 1 meter in air at atmospheric pressure and will produce about 60 ion pairs per centimeter of its path. A 5-m.e.v. α -particle under the same conditions produces about 25,000 ion pairs per centimeter and is stopped in 3.5 cm.

The detection of an α -particle can be accomplished with a relatively shallow chamber with no gas amplification, because 25,000 ion pairs produce a voltage pulse well above the noise level of a pulse amplifier. However, the detection of a few ion pairs produced by β -particles requires a detector with high gas amplification.

The measurement of β - and γ -radiation is made by either of two methods. The first method employs pulse counters in which individual ionizing particles are detected as single ionizing events or "counts." Geiger-Müller counters and proportional counters are representative of this class. In the second method the total ionization produced in an ionization chamber in a given time interval is measured with an electrometer—e.g., quartz fiber, vacuum tube, or dynamic condenser type (γ). The Lauritsen electroscope also falls in this category.

Pulse counters as a general rule are more sensitive than integrating ionization chambers; however, for certain types of radiation—e.g., x-rays, γ -rays, soft β -particles—the ion chamber sensitivity is comparable to the pulse counter.

GEIGER-MÜLLER COUNTERS

The most widely used instrument in tracer studies is the Geiger-Müller counter, primarily because of its simplicity, sensitivity, and availability.

The Geiger-Müller counter consists of a conducting cylinder along whose axis extends a wire of small diameter. The counter is filled with a gas to a pressure of several centimeters of mercury, and a potential of about 1000 volts is applied across the counter with the center wire positive. In the absence of ions in the sensitive volume of the counter no discharge takes place; however, when an ionizing particle enters the counter a few ion pairs are formed and a rela-

tively large current flows through the counter. The voltage pulse is sufficiently large so that very little amplification is necessary to record the pulse. The mechanism of the discharge, which is fairly complex, may be briefly explained in a simplified manner as follows:

The electrons liberated in the sensitive volume of the counter by an ionizing particle are attracted by the positive center wire. When the electrons reach the region of high field intensity close to the wire, sufficient energy is acquired by them between collisions with gas molecules to ionize the gas further and release additional electrons. Each of these electrons similarly produces further ionization, so that a large number of electrons finally reach the wire. If the center wire potential is not too high, the discharge will stop at this point.

A counter operating in this manner is called a proportional counter because the pulse voltage on the center wire is proportional to the number of ion pairs produced by the initial ionizing event. Gas amplifications from 10 to 10,000 can be used with appropriate gases in this type of counter. If the center wire potential is sufficiently high so that gas amplifications of 10^7 to 10^9 are obtained, enough photons are liberated in the discharge to propagate the discharge along the entire length of the center wire. The discharge ceases because the positive ions which were formed in the discharge, owing to their low mobility compared to the electrons, form a positive ion space charge along the center wire, and thereby reduce the field intensity to a point where electron multiplication ceases. Thus every discharge builds up to a constant size regardless of the original number of ions produced.

A variety of designs of Geiger-Müller counters are available, as shown in Figures 1, 2, and 3. Mica end-window counters are most commonly used because of the high geometry obtainable, about 30%, and because the use of thin mica windows from 1 to 5 mg. per square centimeter allows the counting of soft radiation.

A typical gas filling mixture for Geiger-Müller counters is 90% argon and 10% ethyl alcohol at a total pressure of 10 cm. of mercury. The center wire is usually tungsten or kovar wire 5 to 10

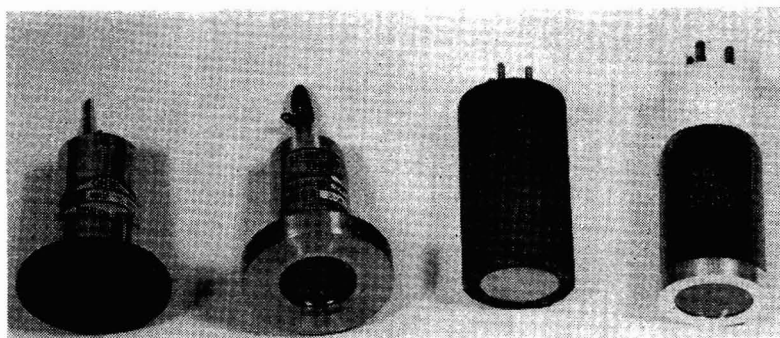


Figure 1. End-Window Geiger-Müller Counters

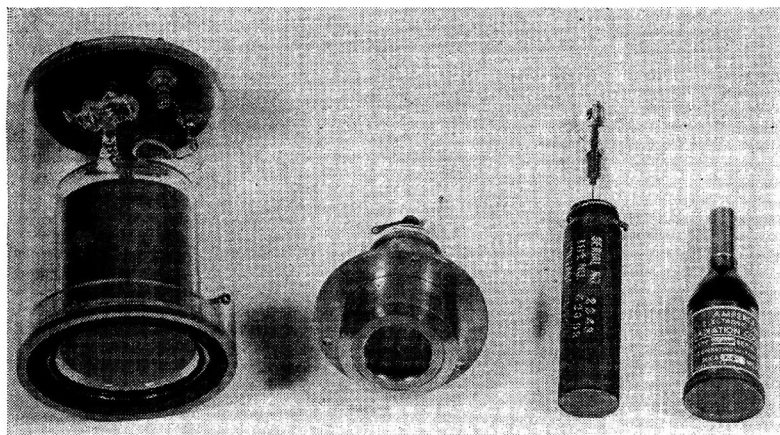


Figure 2. End-Window Geiger-Müller Counters

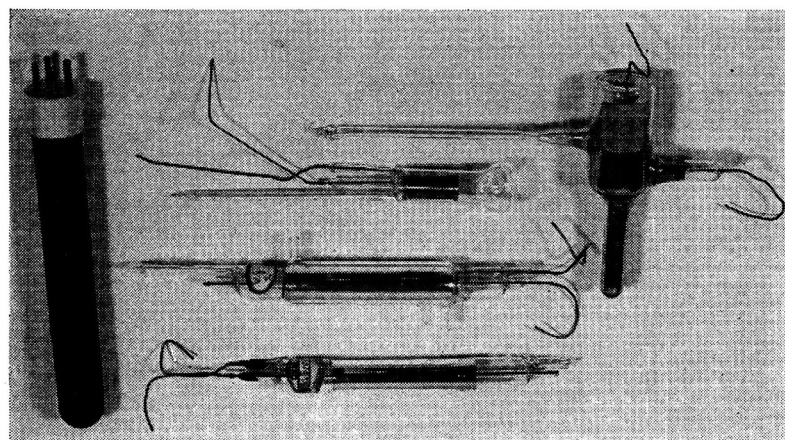


Figure 3. Types of Glass Envelope Geiger-Müller Counters

mils in diameter. Because some of the quenching agent (alcohol) is decomposed in each counter discharge, the life of a counter is usually limited to about 10^8 counts.

One type of Geiger-Müller counter has a thin glass wall about 10 mils thick coated internally by chemical silvering. Another type of thin glass counter is designed so that it can be immersed in liquids containing small traces of radioactivity.

Geiger-Müller counters for detecting γ -rays may have fairly thick glass walls and to improve the γ -efficiency of the counter a screen cathode plated with an element of high atomic number, like bismuth, is used. For example, a ninefold increase in efficiency for a 0.25-m.e.v. γ -ray was obtained by gold-plating the cathode of an end-window counter and placing a gold foil between the mica window and the sensitive volume of the counter. For 1.5-m.e.v. γ -rays the efficiency was only slightly increased.

BETA-PROPORTIONAL COUNTERS

Proportional counters have been developed (1) for precision counting of β -particles, conversion electrons, x-rays, and γ -rays. Voltage plateaus from 200 to 400 volts in length with slopes of less than 1% per 100 volts have been obtained in the proportional region.

Inasmuch as the dead time of the proportional counter is considerably less than 1 microsecond, rates of the order of 1,000,000 counts per minute can be used with a coincidence loss of about 2% at this counting rate. The observed coincidence loss using paired samples is accounted for by the 1-microsecond resolving time of the first scaling stage.

At gas amplifications from 1000 to 10,000 a single ion pair pro-

duced in the sensitive volume of the proportional counter can be detected; consequently, the proportional counter and Geiger-Müller counter sensitivity are identical. Furthermore, as proportional counters are operated at atmospheric pressure, more ions per centimeter are produced by the charged particle than in the Geiger-Müller counter which is usually filled to a pressure well below atmospheric.

The high counting speed allows the following of the decay of radioactive isotope through many more half-lives than is possible with a Geiger-Müller counter. Absorption curves likewise can be taken over a greatly extended range of absorber thickness.

Continuous gas flow proportional counters, as shown in Figure 4 have been operated in the proportional region using either methane or a mixture containing 90% argon and 10% methane. The gas flow through the chamber is such that a 200 cubic foot cylinder of gas will last about 6 months. The sample is placed in the depression in the slide of the chamber and the slide pushed forward so that the sample enters the sensitive volume of the counter. No flushing period is required: counting can begin immediately.

Because the sample is inserted directly into the sensitive volume of the counter, no window or air absorption takes place and a counting yield as high as 70% can be obtained for β -emitters such as C^{14} , S^{35} , and P^{32} . High counting yields such as this are obtained only where the sample has negligible self-absorption and is mounted on a high back-scattering material such as platinum or lead.

A typical voltage plateau taken with the β -proportional flow counter is given in Table I.

Voltage plateaus of this kind are obtained only when a properly designed amplifier is used. As there is a wide distribution in pulse heights from the chamber, it is necessary to use an amplifier that will produce a minimum of overshoot and back-kick on large amplitude pulses and still count small pulses.

Table I. Voltage Plateau for β -Proportional Flow Counter

(Argon-methane mixture)			
Volts	Counts/Min.	Volts	Counts/Min.
1200	225,000	1600	231,000
1300	231,700	1700	231,500
1400	232,400	1800	233,000
1500	231,400	1900	271,000

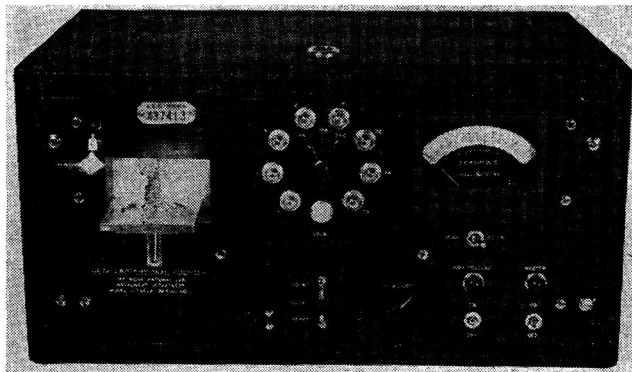


Figure 4. Continuous Gas Flow Beta Proportional Counter

Table II. Counting Rates

Type of Radiation	Geiger-Müller Counter, Counts/Min.	Flow Proportional Counter, Counts/Min.	
		90% Argon 10% CH ₄	CH ₄
Back-ground			
Local gamma-cosmic	25	40	40
C ¹⁴	150 k.e.v. beta	540	4,360
UX ₂	2.3 m.e.v. beta	14,700	22,100
Ni ⁵⁹	6.9 k.e.v. x-ray	24,500	296,000
H ³	17 k.e.v. beta	0	150,000
Cl ³⁵	0.64 m.e.v. beta?	15,600	146,000

Table II gives a comparison between the counting rates obtained with an end-window Geiger-Müller counter having a 3.7 mg. per sq. cm. mica window and filled with argon-alcohol to 10-cm. pressure and the continuous flow proportional counter for various types and energies of radiations.

In the case of the Ni⁵⁹ using 90% argon and 10% methane 65% of the x-rays passing through the sensitive volume of the proportional counter are counted. The H³ sample was a thin film of aluminum oxide on which H₂O was adsorbed.

The life of the continuous flow counter is indefinite, as a continuous flow of gas takes place. Counters of this type have been operated at this laboratory for over 2 years with no change of characteristics. The same continuous flow β -proportional counter can be used for counting α -particles by lowering the center wire voltage to 700 volts, using 90% argon-10% methane mixture. Beta-particles are not counted at this voltage. Alpha-counters of this type have been described (8).

Permanently filled glass-wall silver cathode type counters operating in the proportional region have shown practically no change in characteristics after accumulating 10¹⁴ counts. Table III shows the voltage plateau before and after 10¹⁴ counts. The same counter operated in the Geiger-Müller region showed no plateau.

For all practical purposes permanently filled proportional counters have an indefinite life, assuming no leakage of the envelope. A self-quenching Geiger-Müller counter after only 10⁸ counts will show a plateau slope of 15% or more per 100 volts.

INTEGRATING TYPE IONIZATION CHAMBERS

Integrating type ionization chambers essentially consist of four parts: the collecting volume or ionization chamber proper, the guard ring, the electrode system on which the ions are collected,

Table III. Voltage Plateau

(Argon 67 cm., CO₂ 6 cm., 1-mil wire)

Voltage	Initial Plateau	Plateau after 10 ¹⁴ Counts
1200	19,400	17,800
1245	29,100	29,100
1290	35,700	36,400
1335	38,900	39,500
1380	40,500	40,700
1425	40,600	40,900
1470	41,000	41,200
1500	40,900	40,900
1545	41,100	41,100
1590	41,500	41,500
1635	42,200	41,400
1680	45,100	42,200
1725	48,700	45,600

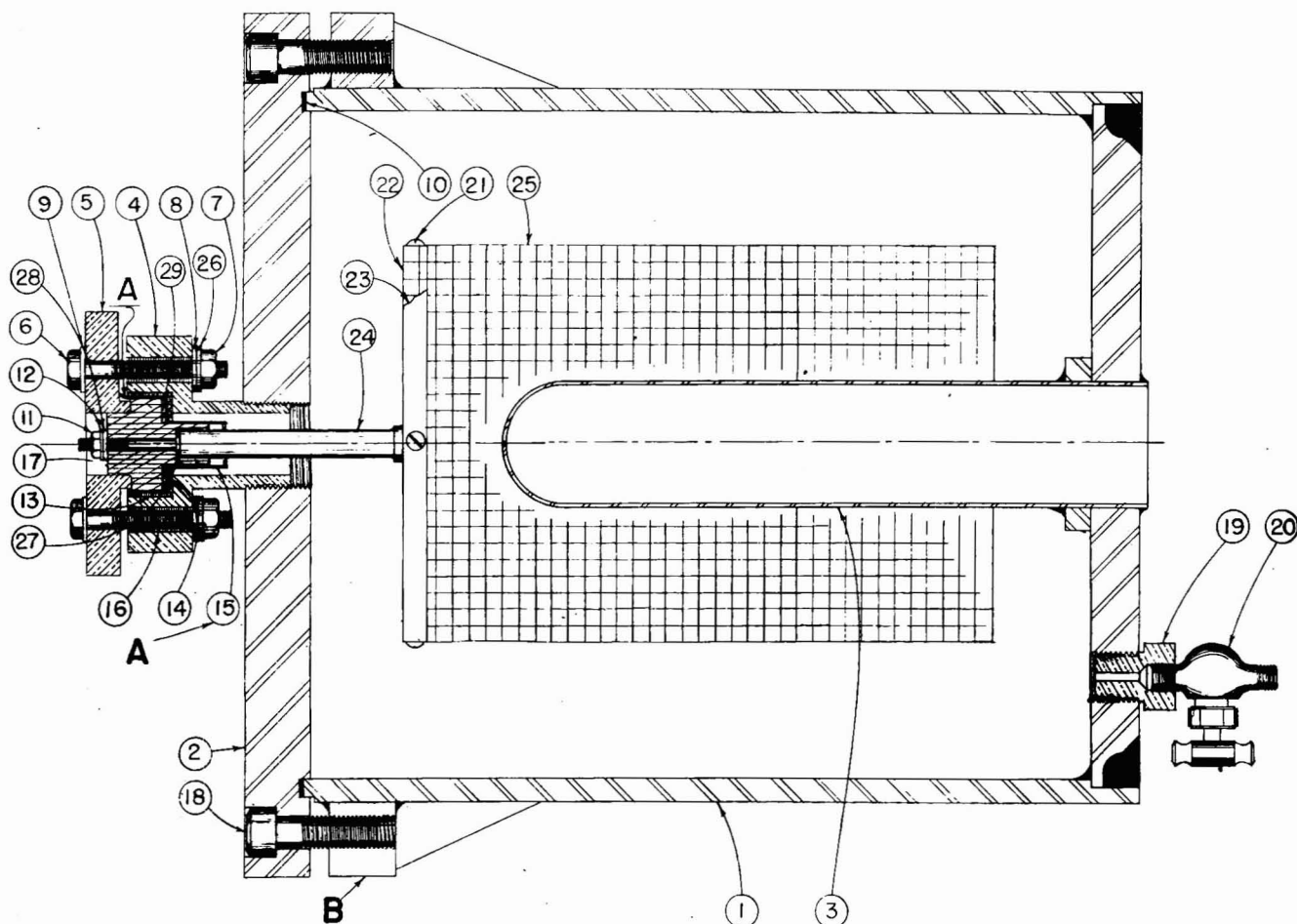


Figure 5. High Pressure Gamma Chamber

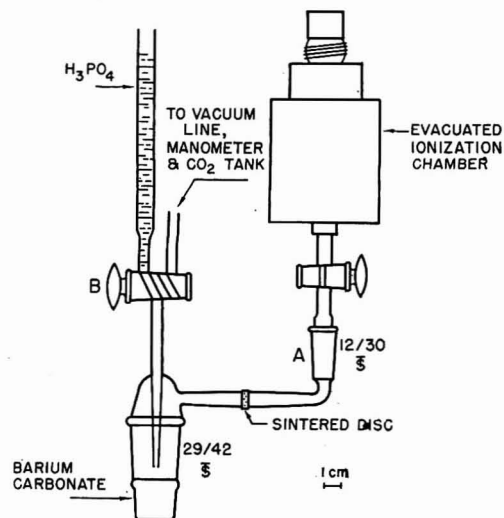


Figure 6. Apparatus for Conversion of Barium Carbonate to Carbon Dioxide

and a measuring instrument to determine the change in potential of the electrode system when the ions are collected.

The collecting volume where ionization occurs may be air or any other gas at or above atmospheric pressure. It is desirable when measuring soft β -particles of low intensity to make the chamber volume small, so that the background of the chamber due to cosmic rays, local radiation, and natural radioactivity of the chamber walls is kept to a minimum.

For detecting γ -rays a pressure of about 40 atmospheres of argon can be used in a chamber designed to measure liquid or solid samples. Such a chamber offers one of the most sensitive and convenient means of detecting γ -rays from samples which may have a volume up to 200 ml.

Figure 5 shows a cross-sectional view of a chamber of this type developed at the Metallurgical Laboratories (9).

The chamber which is 27.5 cm. (11 inches) in diameter and 35 cm. (14 inches) long is made of steel to withstand a pressure of about 40 atmospheres. A steel thimble 30 cm. (12 inches) long and 4.4 cm. (1.75 inches) in diameter with the open end up extends from the center of the top down into the chamber. The thimble is welded to the chamber to retain the filling gas. A basket type of collecting electrode is placed concentrically with the thimble and the chamber wall which is the high voltage electrode. The entire chamber is shielded with 10 cm. (4 inches) of lead.

The sample, which may be liquid or solid, containing the γ -emitter is placed in a test tube and lowered into the thimble of the chamber. The change of potential of the collecting electrode due to the ionization current may be measured with a Lindemann electrometer. However, the dynamic condenser electrometer or a stable vacuum tube direct current amplifier is more convenient to use unless one has a projection system for the quartz fiber of the Lindemann electrometer. The background current of the chamber is about 10^{-13} ampere.

For small currents the rate of drift method is used—i.e., the chamber capacity is allowed to charge up to a definite potential and the reciprocal of the time required to reach this potential is proportional to the ionization current and hence to the γ -activity.

The advantage of the rate of drift measurement is that the total ionization is the same for all measurements and the statistics for each measurement are the same. In addition, the statistical fluctuations in the ion current are integrated over the period of measurement. For higher intensities the steady deflection method of measuring the ionization current is used; one merely measures with the electrometer the voltage drop produced by the ionization current flowing through a high valued resistor—e.g., 10^{10} ohms.

A source emitting 100,000 1-m.e.v. γ -rays per minute gives an ionization current equal to that of the background.

One of the principal advantages of this type chamber is that the sample preparation is exceedingly simple.

One may want to determine the distribution coefficient of a particular compound, labeled with a γ -emitting isotope, between an organic and an aqueous phase. After equilibration the organic phase is separated from the aqueous phase and the two are separately measured in the liquid state. No evaporation step is needed and self-absorption corrections are unnecessary. The observed ion current changes less than 1% if a 1-ml. sample of a γ -emitter is progressively diluted to 100 ml. with water.

The high pressure γ -chamber can be calibrated to give absolute disintegration rates where the γ -ray energy and the decay scheme are known. For example, where I^{131} is used in therapy absolute dosages can be readily measured on the liquid sample which may contain up to 1 millicurie activity.

Because of the simplicity of sample preparation many tracer experiments can be so designed that the use of a γ -emitting isotope in conjunction with the high pressure γ -chamber will yield results in one tenth the time and effort than would be required if a β -emitter were used.

The assay of C^{14} using ionization chambers surpasses manyfold the sensitivity of solid sample counting with Geiger-Müller counters, especially for samples of low specific activity (2-4). If sufficient sample is available to fill the ionization chamber without further dilution, the sensitivity for specific activity of the ionization chamber can be 15 to 20 times greater than for the solid sample counting. Because the measurement is made in the gas phase, usually $C^{14}O_2$ with diluent inactive carbon dioxide, no self-absorption corrections are necessary. Furthermore, other C^{14} labeled gases or vapors such as ethanol can be directly introduced into the chamber for measurement.

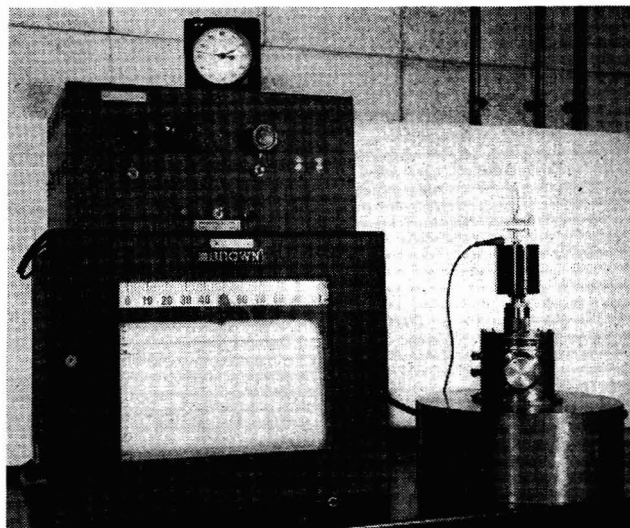


Figure 7. Dynamic Condenser Electrometer and Ionization Chamber

Usually barium carbonate containing C^{14} is acidified with phosphoric acid (85%) and the evolved carbon dioxide after passing through a fritted disk is passed into an evacuated chamber. To sweep out the remaining active carbon dioxide inactive carbon dioxide is slowly admitted until the pressure in the chamber reaches 1 atmosphere. The whole acidification procedure for a 100-mg. barium carbonate sample can be accomplished in about 3 minutes with the apparatus and technique developed by William Leslie, formerly of this laboratory. The acidification apparatus is very simple, as shown in Figure 6.

Over 99% of the active carbon dioxide is transferred to the chamber.

The over-all reproducibility of the acidification procedure and subsequent measurement of the ionization current are illustrated

by the following data, which were obtained by acidifying three 100-mg. samples of barium carbonate:

Sample	Ionization Current, Ampere
1	2.99×10^{-14}
2	2.98×10^{-14}
3	3.00×10^{-14}

With the chamber shown in Figure 7 which has a 275-ml. capacity, a current of about 1×10^{-16} ampere is equivalent to one disintegration per second of C^{14} when the diluent gas is carbon dioxide at 1 atmosphere. The chamber construction has been described (6). The ionization current is not too sensitive to the total pressure in the chamber, as a pressure change of 20 mm. of mercury produces a change of only 1% in the current.

Water vapor if present in the gas in the chamber has no adverse effect on the measurement.

Only 0.2% of the initial activity is absorbed by the brass chamber walls in 24 hours when the diluent gas is carbon dioxide. Air, oxygen, nitrogen, and butane can be used as diluent gases instead of carbon dioxide. The ionization currents per disintegration will be different for these gases—for example, in butane the current is 60% higher than in carbon dioxide.

Using the dynamic condenser electrometer and chamber shown in Figure 7 one disintegration per second in 8 grams of barium carbonate can be detected.

The assay of H^3 can be made with the same instrumentation described for C^{14} .

The Lauritsen electroscopie is a rugged, inexpensive, and simple instrument for the measurement of radioactivity and is useful where moderate intensities are used. Dependent on the energy of the β -particles, it is from 10 to 100 times less sensitive than the Geiger-Müller counter.

SCINTILLATION CRYSTAL DETECTORS

Detection (5) of ionizing radiations by measuring with a photomultiplier the fluorescent light pulses emitted by organic crystals such as naphthalene and anthracene and inorganic crystals such as calcium tungstate, zinc sulfide, alkali halides, when an ionizing radiation passes through them, opens a new field of detection.

For tracer work where β -emitters are used, the crystal detector offers no advantage over previously described instruments. With γ -ray tracers, however, the high γ -efficiency of the crystal, 50 to 100 times greater than a Geiger-Müller counter, makes its use very attractive.

At present the Geiger-Müller counter, proportional counter, ionization chamber, and electroscopie fill the instrumentation needs for the majority of radioactive tracer applications.

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Nucleonics and Analytical Chemistry Symposium

Measurement Techniques of Applied Radiochemistry

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This paper is a survey of the more important practical techniques for the measurement of radioactivity and the principles on which they are based. The discussion is concerned primarily with the requirements for tracer work, in which only relative measurements are needed, but some attention is given to the problem of absolute measurements. Particular emphasis is accorded the types of errors encountered and their reduction and correction. Some original methods of determining corrections for nonlinearity of detectors are presented.

RADIOACTIVITY is of interest to most chemists principally as a tool to be employed, when suited to the purpose, for the solution of problems and the elucidation of matters of interest in their own fields. Applied radiochemistry is in this respect similar to analytical chemistry. Radiochemistry bears another close relation to analytical chemistry by virtue of the fact that many of its applications are analytical in nature. It is thus appropriate in this symposium to consider applied radiochemistry as an analytical tool. Applications of this tool are described in some of the papers in the symposium; others, including this, are concerned with various aspects of the tool itself.

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In describing the techniques of measurement in applied radiochemistry an attempt is made to indicate the limitations to the attainable precision. The over-all accuracy of any application of radiochemistry can be no greater than that of the measurements involved. Crude or approximate measurements suffice for many purposes, but high precision may be demanded on occasion. Like the research analytical chemist, the radiochemist is constantly striving to increase the scope and accuracy of his methods, with confidence that any such improvement will sooner or later find profitable application. Consequently, a considerable portion of this discussion is devoted to methods of reducing errors.

The selection, adaptation, and operation of radiometric instruments, although an integral part of the technique of radioassay,

have been reviewed in this symposium (18), and are not discussed here.

PREPARATION AND MOUNTING OF SAMPLES

Requirements of Samples. The measurement of radioactivity involves the placing of the active material or a sample therefrom near a detector and noting the quantitative effect of the former on the latter. The active substance must be free of interfering substances, in a suitable chemical and mechanical form, and disposed in a definite and fixed position relative to the detector. More specific requirements depend on the nature of the activity and the purpose of the measurement. In virtually all applied radiochemistry, including isotopic tracer experimentation, isotope dilution analysis, and radioactivation analysis, relative intensities of two or more samples are all that need be determined, thus making absolute measurements unnecessary. The principal requirement, is, therefore, reproducibility. Absolute reproducibility in sample preparation is highly desirable, for then the detector response is strictly proportional to the sample activity, and the proportionality factor cancels out in the ratios. If this is not possible, reproducibility should be maintained in all but one or a few respects, and the effects of the variable factors determined and corrected for.

A chemical assay of the active element or compound is often required in addition to the radioassay; it is then desirable to prepare the sample in a form suitable for gravimetry. If the chemical form of the active element must be preserved, as in the case of organic compounds of C^{14} , H^3 , and S^{35} , which are to be used unchanged after their measurement, additional restrictions are imposed on the preparation for measurement. The prepared sample must be sufficiently stable that changes before or during measurement do not occur, and that active material is not lost from samples to contaminate detectors and working areas.

For specialized physical measurements, such as of radiation energies and absolute intensities, the preparation must in addition minimize the disturbing effects of absorption, scattering, and secondary radiations. This generally requires that the sample be of very small bulk ("weightless" or "carrier-free") and deposited uniformly in a small or well defined area, and that materials which would scatter radiations be absent. To eliminate scattering by the support, extremely thin supporting material must sometimes be used.

Manipulation of Radioactive Substances. Because every radionuclide is an isotope of a particular chemical element, with which it shares its chemical properties, chemical techniques are of especial importance in the handling of radioactive substances. A chemical separation from inactive, and occasionally active, concomitants generally precedes the activity measurement. Ordinary analytical techniques and reactions form the basis for most radiochemical separations.

Modifications are often required, however, by the small amount or low concentration of the active element. There are many advantages to working on a small scale, making microchemical techniques of particular importance (125, 135). Carrying of a microconstituent by coprecipitation with a macroconstituent (56), solvent extraction, volatilization, adsorption, ion exchange, electrodeposition, and electrochemical deposition, are useful for handling very low concentrations of material (135).

Further modifications may be necessitated by the radiations. If these are intense and penetrating, shielding and remote-control equipment are required (67, 96, 148). Even for nuclides with nonpenetrating radiations, dangers of skin exposure and body intake exist. All work with appreciable quantities of radioactivity should be done with rubber gloves, protective clothing, and adequate ventilation to remove active vapors, dusts, and sprays. Although the amount of activity used in a single radioassay or tracer experiment is generally too small to be by itself a health hazard, and less elaborate precautions may suffice, this

may not be true of stock solutions of active materials and other sources of tracers.

Of scarcely less importance is the danger of contamination of laboratories, equipment, and detecting instruments by active materials, which is still present at activity levels too low to be dangerous to health. Establishment and enforcement of suitable regulations and careful attention to cleanliness of operation are integral aspects of the proper technique of working with radioactivity (67, 109, 111, 112, 144, 149).

Preparation of Solid Samples. For the measurement of most radionuclides, the use of solid samples has proved convenient. The active material must be spread in a uniform layer over a definite area. Solids may be powdered to a particle size small relative to the thickness of the layer desired and to the range of the radiations, and spread wet or dry. Thin uniform layers of powders may be prepared by sedimentation from air or from a volatile liquid which is later evaporated. Many inorganic solids form coherent deposits when spread as slurries in water or alcohol and dried. These techniques have been used for barium sulfate (62), barium carbonate (33, 82, 141, 155, 157, 158), magnesium ammonium phosphate hexahydrate (68, 95), and numerous other compounds. The residue of ashed biological tissues may be spread in the same manner. If the deposit is not coherent but tends to fall apart and flake off, it may be stabilized by the use of a suitable binder (collodion). Alternatively, the deposit may be held in place with a covering layer of cellophane, Scotch tape, aluminum foil, or similar material.

The sample is frequently obtained in a solid form by precipitation from solution. By suitable choice of precipitating agent, a separation from bulk inert materials and an incorporation into a form suitable for measurement may often be achieved simultaneously. If the precipitate is separated by centrifugation, it can be transferred as a slurry with a small transfer pipet, which need be no more than a glass tube drawn to a point at one end and with a dropping bulb at the other, and mounted as described above.

A method used for β -active rare earth compounds (104) illustrates a combination of the above techniques. (Pm^{147} activity used in this work was purchased from the United States Atomic Energy Commission.)

The rare earths were precipitated as oxalates, filtered, washed, transferred with the paper to a crucible, ignited to oxides, and ground in the crucible with a stirring rod. A portion was weighed into a flat 3.8-cm. (1.5-inch) diameter aluminum pan, moistened with 1 ml. of 2% collodion in methanol, spread evenly with a microstirring rod, evaporated slowly to dryness under a heat lamp, and heated strongly with the lamp for a few minutes. U_3O_8 , prepared by ignition of uranyl nitrate and grinding in a mortar and pestle, was similarly mounted in a machined depression in an aluminum plate and covered with Scotch tape for use as a source of constant β -activity.

If the precipitate has suitable characteristics, it may be filtered onto a flat filter paper or sintered glass disk, washed with a volatile solvent (acetone, methanol, ether, etc.), dried, and measured on the filter medium. This technique has been used extensively for C^{14} in the form of precipitated calcium carbonate, barium carbonate, or lithium carbonate, and several arrangements for carrying out the filtration and mounting the precipitate have been described (1, 6, 7, 26, 128, 131). For S^{35} , barium sulfate precipitates have been used (146), but benzidine sulfate has been found to give better filtration characteristics (63). Magnesium ammonium phosphate hexahydrate is suitable for assay of P^{32} (101), silver iodide (136) and palladium iodide (12) for radioiodine, and metallic arsenic for As^{73} (64). Suitable analytical precipitates can be found for most of the elements. Flocculent precipitates which are highly hydrated, such as the hydroxides of most metals, tend to give unsatisfactory deposits, because on drying they contract into a number of isolated dense particles which give high and variable self-absorption and tend to flake off readily. Some microcrystalline precipitates, such as the silver halides, are not completely retained on the usual filter

media under suction. This may cause no difficulty if the specific activity (activity per unit weight) will give sufficient information, and if the weight of material on the filter can be determined.

Evaporation of solutions in dish- or cup-shaped containers; or for small amounts, on flat surfaces, is convenient. The method is limited to nonvolatile activities, and gives good results only when the total amount of nonvolatile material present is small. When appreciable amounts of solids are present, they tend to deposit in a ring on the outside of the evaporating solution or in the corners of the container, giving uneven and nonreproducible deposits. It is sometimes possible to improve the spreading by stirring with a thin glass rod during the last stages of evaporation. With highly active solutions a small aliquot may contain sufficient activity for accurate assay and still have insufficient solids to cause interference. For such aliquoting, calibrated micropipets in the 10- to 500-microliter range (137) are useful. Filter, lens, or blotting paper is sometimes impregnated with the active solution and dried (81, 82).

An adaptation of this technique to less active solutions involves the separation and concentration of the activity by precipitation and centrifugation, dissolution of the precipitate in a small volume of suitable volatile solvent, transfer of the solution, and evaporation. When the whole operation is carried out on a micro or semimicro scale, the total amount of precipitate will generally be insufficient to cause difficulties even though the distribution may be irregular.

When large amounts of solids are present, uniform deposits may sometimes be obtained by the use of special reagents. As an example, tetraethylene glycol added to an evaporating solution of uranyl nitrate results, after ignition, in a uniform layer of U_3O_8 (70). The action is probably due to the combined effect of surface tension alteration and the fact that on concentration a finely divided precipitate forms and settles out uniformly. This reagent is said to work similarly for other elements, and there should exist other substances which are effective in this manner.

Electrodeposition onto a flat surface gives excellent deposits for many metals. It is often possible to achieve quantitative and uniform deposition over a definite area. Among the elements for which this technique has proved particularly useful are iron (53, 57-59, 120, 129, 152), gold (36), and uranium (23, 25, 70, 79).

The cathode may be a disk of copper, iron, gold, or platinum supported under compression at the bottom of a glass tube; the tube serves as the electrolysis cell, and a rubber or neoprene gasket between the tube and cathode may be used to seal the joint. Alternatively, the disk may be covered on one side with a layer of lacquer (Glyptal) and dipped into the solution. A tubular cathode so covered on the outside, or used as the wall of the electrolysis cell, provides a relatively large area for large samples, and can be slipped over a thin-walled counter tube for efficient measurement.

Sublimation with condensation on a cold surface gives good deposits, but is not often used for routine assays because of the difficulty of making quantitative transfers. An exception is the case where the process being studied is one of volatilization (39). An important application is to the preparation of very thin and uniform layers for physical measurements, particularly of α -radiations (70).

Deposition of nascent atoms, such as those recoiling from α -decay, gives good but nonquantitative deposits, and has been extensively used in studies of the natural radioelements. Recently the method has been applied to the artificially produced radioactive chains among the heavy elements (50, 143). Here again the method is not quantitative and has only special applicability.

Mounting of Solid Samples. The container or support for the sample may be flat or shaped, and made of any material that is chemically inert under the conditions of use.

Flat foils or disks are preferable for small samples; several tenths of a milliliter of a liquid can be held in place by surface tension, and somewhat larger amounts can be retained by a ring

of lacquer (Zapon) or grease (high-melting silicone). One-inch microscope cover glasses are cheap and useful when the deposit need not be heated to a high temperature. Aluminum, brass, and copper foils and cellophane sheets are applicable when corrosive liquids are not involved, and stainless steel can be used for many acid solutions. Platinum is almost universally applicable, but because of its expense must be cleaned and re-used except in laboratories of ample means. Disks of Teflon, which is chemically inert and withstands temperatures considerably above the boiling point of most aqueous solutions, have also been used.

For larger amounts of solids or solutions, hollowed containers can be employed. Watch glasses, especially the 2.5-, 3.5-, and 5-cm. (1-, 1.5- and 2-inch) sizes, are useful as well as inexpensive, but attention must be given to variations in shape and thickness. Porcelain flat-bottomed ashing capsules have larger capacities and permit ignition of filter paper from a precipitate before measurement, or the determination of the gross activity of a biological tissue after ashing. The potassium content of porcelain results in an increase in the background because of the natural β -activity of that element, and this must be determined and corrected for. Shallow cups of aluminum, plated steel, and copper foil can be mass-produced by stamping and are available commercially. It is claimed that a series of concentric grooves or ridges in the flat bottom of such a cup gives greater reproducibility when solutions are evaporated (91, 140).

When back-scattering by the mount is objectionable, a thin film of low atomic number may be used. Thin aluminum foil, although not ideal, sometimes suffices. Extremely thin and tough films of plastics (Zapon, polystyrene, Formvar, nylon) may be made by dropping a small amount of a solution of the plastic in a suitable solvent on the surface of water or a glass plate, and allowing it to spread and evaporate (21, 47).

An arrangement is needed for holding samples in a definite position relative to the detector during measurement. Counters and ion chambers for routine use are generally equipped with an arrangement having one or more shelves or sets of slots in which sample holders of a standard size can be placed. Flat flexible samples are sometimes wrapped around cylindrical counter tubes.

Liquid Samples. Radionuclides emitting sufficiently penetrating β - and γ -radiations are conveniently assayed in solution, provided sufficient activity is available to overcome the additional self-absorption of the solvent. A flat vessel containing the solution placed beneath the instrument provides a simple though inefficient arrangement (139). More effective is a thin-bottomed vessel which can be placed on the window of a counter tube (100). Several types of dipping counter tubes (9, 10, 59, 153) and tubes surrounded by hollow jackets (11, 92, 107, 117, 150) have been described. The most convenient jacketed

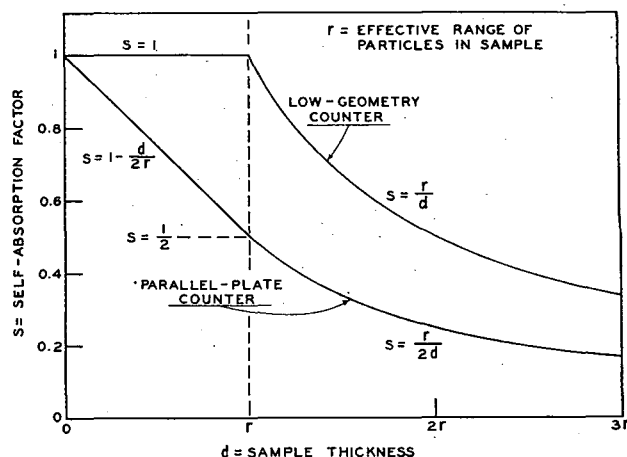


Figure 1. Theoretical Self-Absorption Curves for Alpha-Particles

counters have a tubulation at the bottom for the solution and another at the top for controlling the flow of liquid by suction and pressure.

It is unfortunate that the three most important radiotracers for organic chemistry, H^3 , C^{14} , and S^{35} , have radiations too soft to make assay in solution convenient. For the latter two the method would be satisfactory if the diaphragm separating the solution from the counter interior had a thickness of only a few milligrams per square centimeter, but with thick layers of liquid an excessive amount of activity would be required. A suitable vessel designed to confine the liquid to a layer a few tenths of a millimeter thick would have many useful applications for the measurement of soft β -emitters.

Scintillations have been observed from naphthalene in contact with tritium (147), suggesting that if an efficient way of causing tritium to excite luminescence in liquids could be found, photoelectric scintillation counting might be adapted to the assay of tritium in solution.

Gaseous Samples. Similar methods have been used for the measurement of gaseous radioelements and radiocompounds. In studies of the noble gases among the fission products, thin-walled cells were used to hold the active gases before the window of a Geiger counter tube. For the measurement of C^{14} -containing gases, mica-window counters have been equipped with gas cells having as one wall the counter window, so that only this separates the activity from the detector (89). Because of the low density of gases, self-absorption is small even with cells of several cubic centimeters volume, but only a small amount of material can be put into the cell at one time, and high specific gravity is consequently necessary. As carbon is often present in gaseous compounds, and in any form can be converted into carbon dioxide, this method is well adapted to routine assay of C^{14} samples.

The introduction of active gases into ionization chambers or counters has been used for many years for radon, thoron, and actinon. It is especially useful for emitters of soft β -radiations, and is in fact the only presently feasible method for the assay of tritium. The tritium-containing hydrogen is generally converted to the elementary form, although small concentrations of water vapor can be tolerated in Geiger counters, and a number of other volatile hydrogen compounds can be used (2, 15, 38, 45, 61, 66, 77, 80, 93, 118, 122). Applications to C^{14} have also been made, using both ion chambers and counters (65, 94, 131, 138). The discovery of conditions under which Geiger counters can be operated with high partial carbon dioxide pressures (22, 106) provides a sensitive and general method of C^{14} assay even for low specific activities.

SAMPLE ERRORS AND CORRECTIONS

The errors to which radioactivity measurements are subject can be classified as random and systematic. As in scientific work in general, an effort should be made to determine and correct for any systematic errors. These can be further divided into sample errors and instrumental errors.

Under sample errors are included those due to variations in the sample itself and in its preparation, as well as variations in its disposal relative to the detecting instrument. Inasmuch as the results of applied radiochemistry are always derived from ratios of activity measurements, the correction for such variations is in principle simple. All that is needed for this is an empirical determination of the relative effects of each of the variables.

Effect of Sample Thickness. The factor that varies most frequently in routine radioassays is the thickness of the sample. If this is an appreciable fraction of the range of the radiations in the sample material, the resulting absorption and scattering of radiations will affect the observed intensity. This effect may be expressed in terms of a self-absorption factor, s ; which is a function of the sample thickness, d , and is unity for zero thickness. In general, s decreases as d increases, as a result of the absorption of the radiations from lower layers in upper layers through which

they must pass. The importance of the effect will, of course, depend on the ease with which the radiations are absorbed, being greater for α -emitters and soft β -emitters than for hard β -emitters and γ -emitters.

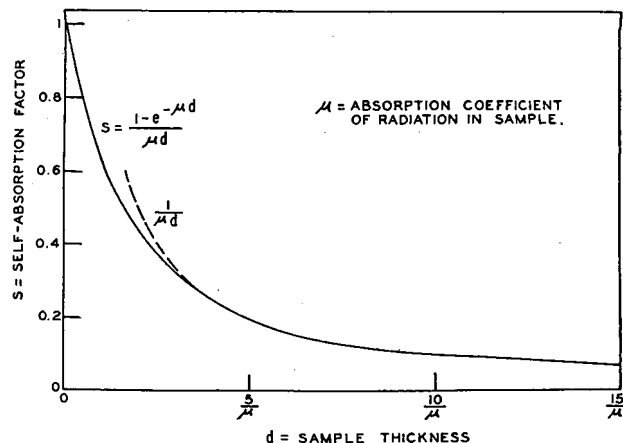


Figure 2. Theoretical Self-Absorption Curve for Monoenergetic Gamma-Radiation (Low Geometry)

For the empirical determination of $s(d)$, several equivalent methods are commonly used:

1. A series of samples is prepared by the adopted technique, using the same amount of activity but a different amount of carrier or inert material for each, and a plot of observed intensity versus sample thickness or weight is made. If this curve is normalized to unity at $d = 0$, it will be the desired self-absorption factor curve. When the sample technique does not permit the preparation of weightless samples, an extrapolation to zero thickness must be made, the exact way this is done being immaterial; alternatively, the factor can be taken as unity at some point on the curve.

2. A series of samples is prepared using varying amounts of material of constant specific activity, and the observed intensity is plotted against thickness. This curve can be transformed to one of self-absorption factor by dividing each ordinate by its abscissa and normalizing to unity as before. The literature contains numerous examples of the application of these methods (6, 20, 43, 54, 55, 60, 62-64, 78, 95, 120, 121, 125, 129, 141, 156-158).

3. This method involves the addition of successive layers of inert sample material or other absorber to a thin layer of the activity, and calculating the shape of the self-absorption curve from the observed absorption curve (20, 54, 78). This procedure gives correct results only if the sample, absorber, and backing have identical scattering and absorption characteristics and other precautions are observed.

Simplifying assumptions regarding the nature of absorption of various types of radiations are useful for estimating the magnitude of the self-absorption factor in specific cases.

Figure 1 illustrates schematically the self-absorption of monoenergetic α -particles in the two most important types of α -counters. The advantage of the "low geometry" arrangement is obvious. Curves actually obtained are modified by straggling and scattering. The corresponding curves for current- or charge-measuring ionization chambers are different. Self-absorption of α -particles has been discussed in detail (16, 40, 43, 83, 115).

Figure 2 shows the self-absorption curve for γ - or x-radiation in the simplest case. In practice the situation may be complicated by oblique passage of radiations through the absorbing layers, and by transition effects. A number of special cases of absorption and self-absorption of γ -radiation have been worked out, principally in connection with radium sources (see 41 for summary).

Beta-radiation is, fortuitously, absorbed in an approximately exponential manner, so that the self-absorption curve (Figure 3) resembles that of monoenergetic γ -radiation. Empirically, it is

found that for a simple β -spectrum the apparent absorption coefficient, α (defined by $s = 1/\alpha d$ for thick layers), is related to the maximum electron range, r , by $\alpha \approx (5-10)/r$, the numerical factor depending on the shape and energy of the β -spectrum, the type of detector, and details of the geometry (63, 64, 97, 141). Figure 4 illustrates the type of curve obtained in method 2. The intensity "saturates" for practical purposes appreciably before the thickness equals the range, beyond which the layer is said to be "infinitely thick."

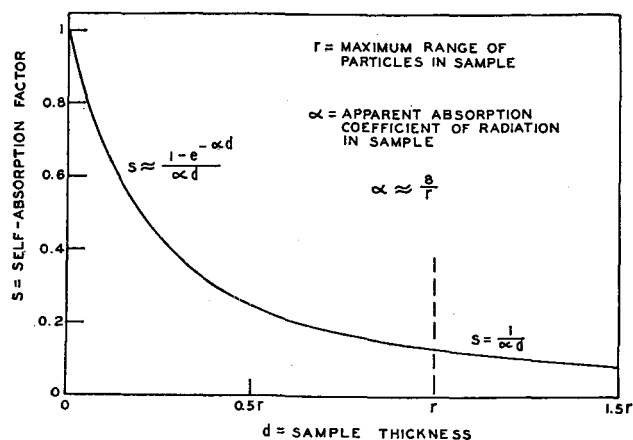


Figure 3. Semitheoretical Self-Absorption Curve for Beta-Radiation (Low Geometry)

The effect of sample thickness on the apparent strength of a sample emitting β -radiation is actually a complex combination of the effects of scattering and retardation of electrons (54, 158). As a result of "self-scattering" within the sample, electrons have a somewhat greater tendency to emerge at large angles to the surface than at small angles, and the net effect in some cases is an initial increase rather than a decrease in the "self-absorption" factor (52). In other cases, self-absorption and self-scattering roughly compensate, and the observed intensity of a sample of constant activity is nearly independent of sample thickness over an appreciable range of thicknesses; this may conveniently eliminate the need for determining the thickness of the sample as long as it is known to be within certain limits (78, 101, 129). Because the exact shape of the curve depends upon so many factors, it is essential that it be determined empirically, rather than calculated, when exact measurements are to be made.

Variations in Other Conditions of Measurement. The apparent intensity of a sample depends also on other factors, such as distance from the detector, area and manner of spread, shape and material of support, chemical form, thickness of covering or other intervening absorbing materials, etc. It is frequently desirable intentionally to vary the distance or introduce absorbers in order to adjust the intensity to within the best operating range of the instrument. In all such cases, it is only necessary to intercompare the various geometries used and apply appropriate conversion factors. Some caution must be observed, however, for variation in one condition of measurement—for example, sample-detector distance—may change the effect of varying another—for example, sample thickness.

In the assay of radioactive liquids, where the sample shape and size are always the same, self-absorption is a function of the composition of the liquid, and the relationship must be determined. For β -radiation, the most important factor is the density, but for photon radiation the atomic numbers of the constituent elements are also significant.

Careful selection of measurement conditions may minimize the effects of certain variables. Use of a relatively large sample-detector distance will cause variations in the distribution of the sample to be less important; this must, of course, be weighed

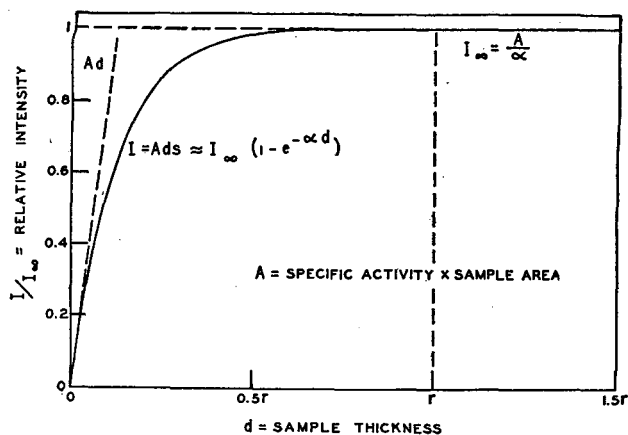


Figure 4. Observed Intensity vs. Sample Thickness for Beta-Active Material of Uniform Specific Activity

against the lowered efficiency of detection. When flat samples are measured with circular window counter tubes, the dependence on sample distribution is greater for samples of large area than for those of small area. Hence, unless the spreading is uniform, the area should be made as small as possible consistent with the increased self-absorption. If a sample emits both soft and hard radiations, the former are generally more subject to variations in self-absorption than the latter, and greater reproducibility can be obtained by introducing an absorber to limit the detection to the latter.

Variations in self-absorption can be eliminated by use of either extreme of sample thickness. If the amount of sample is always small, it may be possible to spread it over such an area that self-absorption is negligible. On the other hand, if the sample is always "infinitely thick," its apparent activity is independent of the actual thickness, and is directly proportional to the specific activity. In many types of experiments, including isotope exchange studies and some biological investigations, specific activity measurements lead directly to the desired result. If the total sample is insufficient to give a layer thicker than the range, it may even be desirable to dilute it before measuring in order to achieve the advantages of infinitely thick layers.

Chemical Yield Variations. Low chemical yields in the preparation of samples are generally associated with large yield variations and consequent uncertainty in the yield. When nearly perfect yields are not assured, a chemical assay may be required in addition to the radioassay. A single determination of the amount of material in the measured sample permits calculation of the specific activity. To find the total activity, a determination or independent knowledge of the total amount of the active chemical species is also needed. This procedure has been extensively used in determinations of fission yields. To the mixture of activities, a known amount of carrier element is added, then separated in the necessary state of chemical and radiochemical purity but without attention to yield. The isolated sample is weighed, and the activity measurement is corrected by multiplying by the ratio of added element to recovered element.

Radioactive Decay and Growth. Corrections for radioactive decay of a single active nuclide of well-known half-life can be simply and accurately calculated. Complications arise when chain disintegrations exist, but these are rarely encountered in applied radiochemistry. Exceptions are found in the naturally occurring radionuclides such as ThB (Pb^{212}), ThX (Ra^{224}), and UX₁ (Th^{234}), and certain of the fission products, which are frequently used as isotopic indicators for their respective elements. In most such cases the active descendants are short-lived, and it is best to wait a sufficient time after the sample preparation for transient equilibrium to become established before making the measurement. A different sort of difficulty is encountered with

preparations containing active isotopes. Mixtures of Fe⁵⁵ and Fe⁵⁹ are frequently encountered. Because the isotopes decay at different rates (half-lives 4 years and 43 days in this case) and have different radiation characteristics, the apparent decay rate of the mixture will vary with time and with the conditions of measurement. Decay corrections cannot be calculated easily, and all measurements are best compared with the activity of a standard sample of the same preparation.

INSTRUMENTAL ERRORS AND CORRECTIONS

Background. Every instrument used for radioactivity measurements exhibits a background response in the absence of active samples. This is due in part to radioactive contamination of construction materials, in part to cosmic radiation, and on occasion in part also to incomplete shielding from nearby radioactive materials, cyclotron, or pile. The background must be determined and subtracted from all measurements.

Residual errors remain, however, because of the variability of the background. Besides the random fluctuations, there are also real variations in the mean background intensity. In addition to possible variations in local radiation sources, the intensity of cosmic radiation at any one place is subject to fluctuations of several per cent (see 145 for summary). These fluctuations include periodic, irregular, world-wide, and local ones. Recognized periodicities coincide with those of the solar day (amplitude ~0.2%), the sidereal day (amplitude ~0.05%), the period of rotation of the sun (amplitude ~0.4%), and the year (amplitude ~1%). Variations correlate with variations in barometric pressure (~-4% per centimeter of mercury), atmospheric temperature (~-0.2% per °C.), the earth's magnetic field (normal variations of ~1%, increasing severalfold during magnetic storms), and solar activity (on rare occasions causing variations of >10%, 46). The various effects are not independent, and differ at different altitudes and magnetic latitudes. Most of the measurements of cosmic ray intensities have been made either with large ionization chambers, often with massive shielding, or with sets of counters in coincidence arrangements to isolate certain classes of cosmic ray events, and measurements with single counter tubes in environments similar to those used commonly for radioactivity measurements appear not to be so extensive. However, it is easy to notice variations of several per cent in background measurements of sufficient duration to reduce random fluctuations to

less than 1%, and it is clear that cosmic ray variations introduce an uncertainty of the order of magnitude of 5% of the background in routine radioassays.

Reduction of residual errors due to the background is accomplished by making it as small and as constant as possible. Both objectives are achieved by using pure and clean materials of construction and by shielding from cosmic rays and local radiation sources. One to 2 inches of lead are commonly used for shielding, and are generally satisfactory unless intense local sources are present.

Elimination of some of the effect of cosmic ray fluctuations on ionization chamber backgrounds is sometimes accomplished by the use of twin chambers, one of which is exposed to the sample and the other to the background only; the reading of the latter is subtracted electrically or arithmetically from that of the first. Because both are exposed to the same average cosmic ray flux, real fluctuations will tend to cancel. However, random fluctuations will be increased, and for short measurements this arrangement is actually a disadvantage (42).

With counters, the background can be reduced and cosmic ray fluctuations, both real and random, largely eliminated by use of auxiliary cosmic-ray counters connected in anticoincidence with the sample counter (3, 14). Penetrating mesons or Auger showers usually trip at least one of these blocking counters whenever they trip the main counter. A reduction of the background counting rate by a factor of 5 has been reported with such an arrangement. The residual background should fluctuate more nearly according to the law of random events.

Nonlinearity of Detector Response. All radioactivity detectors exhibit a continually decreasing sensitivity with increasing intensity of radiation. The response curve is thus not linear, as it would be for a perfect instrument. With ion chambers and electroscopes, the effect can be due to volume recombination of ions and to mechanical sluggishness. With counters, it is due to the finite resolving time, or interval that must separate two events if they are to be separately registered. This "dead time" is due to space charge effects in Geiger counters and to ion mobilities or electrical circuit limitations in ionization and proportional counters.

Figure 5 shows experimentally determined response curves, or plots of recorded rate *R* versus true rate *N*, for several counters of different types. The straight line of unit slope is that for a hypothetical perfect instrument. Calculated curves according to two simple theories involving a constant resolving time τ are also shown. The nature of the deviations from linearity is shown better in Figure 6, in which the fractional correction $f = (N - R)/R$ is plotted against *R*. The latter is given in units of $1/\tau$ in order to give the curves a common initial slope of unity. (τ is here defined in terms of the initial slope, 84.)

The theoretical expressions considered are:

$$N = R/(1 - \tau R) \quad (76, 130) \quad (a)$$

$$N = R e^{\tau R} \quad (133, 151) \quad (b)$$

Equation *a* assumes a constant dead time after each recorded event, and Equation *b* assumes a constant dead time after every event, whether recorded or not. Two mathematical approximations are:

$$N = R + \tau R^2 + \frac{1}{2}\tau^2 R^3 \quad (71) \quad (c)$$

$$N = R + \tau R^2 \quad (75, 84, 85, 105) \quad (d)$$

The corresponding expressions for *f* are:

$$f = \tau R/(1 - \tau R) \quad (a')$$

$$f = e^{\tau R} - 1 \quad (b')$$

$$f = \tau R + \frac{1}{2}\tau^2 R^2 \quad (c')$$

$$f = \tau R \quad (d')$$

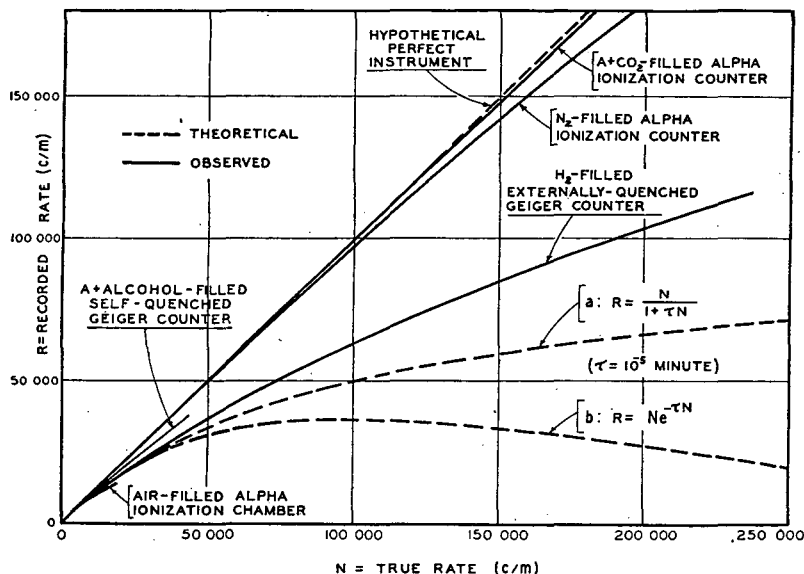


Figure 5. Counter Response Curves
Data from (84-87)

It is seen from Figure 6 that none of the observed behaviors corresponds to either of the simplified theoretical expressions. It has been shown that the average dead time of Geiger counters decreases with increasing counting rate (8, 29, 32, 51, 85, 90, 110), which means that their f curves should always lie below curve a' . On the other hand, because of the "piling-up" of pulses in ionization counters, their curves should always lie about curve b' . All counters so far studied by the writer bear out these expectations.

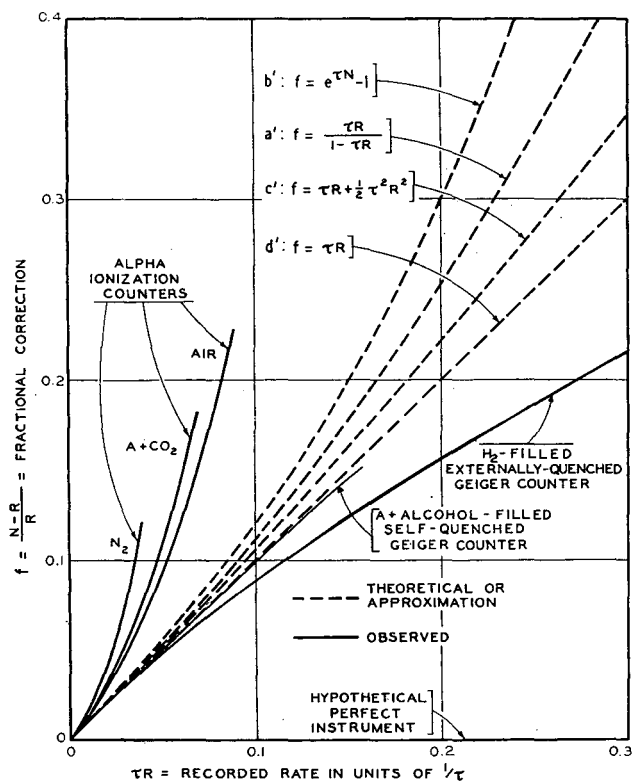


Figure 6. Fractional Correction Curves for Counters

Although the error introduced by nonlinearity is finite at all counting rates, it is small at low rates, and for crude measurements or for low activity levels it may be permissible to ignore it. For accurate work, and for utilization of the full range of usefulness of an instrument, it is necessary to determine and apply corrections. Three practical methods of determining nonlinearity corrections are described here. Several others have been used or proposed, but most of them are inaccurate for various reasons. The methods which follow are not restricted to counters, but should be applicable to a fairly large class of measuring instruments.

METHOD OF PAIRED SOURCES (108). Two radioactive sources of approximately the same strength are obtained or prepared. Four measurements are made:

$$\begin{aligned} R_A &= \text{recorded rate of source A} \\ R_B &= \text{recorded rate of source B} \\ R_C &= \text{recorded rate of combined sources} \\ b &= \text{background rate} \end{aligned}$$

Sources A and B are measured in different but roughly equivalent positions, and each must be in exactly the same position during each of the two measurements involving it. This is most conveniently done by making the measurements in the order R_A, R_C, R_B , leaving A in place between the first two and B in place between the second two measurements (72). When either is measured alone, a dummy source will compensate for scattering by the missing source. Equal time should be given to the measurement of R_A, R_B , and R_C (13).

For any single-parameter relationship of the type $a-d$, it is possible to calculate a value of τ such that the sum of the separate source measurements equals the combined source measurement after each has been corrected for nonlinearity and background. Several equations for doing this have been developed, corresponding to cases a (13, 84, 123-125), b (27, 99, 124, 125), c (71), and d (75, 84, 85, 93, 105). That for case d is particularly simple:

$$\tau = (R_A + R_B - R_C - b) / (R_C^2 - R_A^2 - R_B^2) \quad (d'')$$

The value of τ so calculated will not be the true value unless the instrument follows the equation used. Errors in the determination and application of τ do not compensate. However, at low rates all the equations become identical. Consequently, if measurements are limited to rates such that the correction does not exceed a few per cent ($\sim 10\%$ for Geiger counters, $\sim 2\%$ for α -counters), the residual error after application of the correction will generally be below 1 or 2%. Equations d and d'' are the easiest to work with, and moreover d appears to represent the actual behavior of Geiger counters better than any of the other simple single-parameter relationships. d and d'' are therefore recommended for routine work when first-order corrections will suffice. A nomogram may be used for the calculations (93).

METHOD OF MULTIPLE PAIRED SOURCES (84, 85). An extension of this method involves the taking of several sets of paired-source measurements at different intensity levels.

The relationship between the true and recorded rate is expressed by a power series:

$$N = R + \tau R^2 + \nu R^3 + \varphi R^4 + \dots \quad (e)$$

$$f = \tau R + \nu R^2 + \varphi R^3 + \dots \quad (e')$$

The number of parameters needed depends upon the accuracy required and the range used of the instrument, and can generally be determined by a simple preliminary examination of the data (84). Two (τ and ν) generally suffice, and only the two-parameter case will be described here.

The calculation of τ and ν from the multiple paired-source data is done by an application of the method of least squares, and only the resulting formulas need be given. For each set of paired-source measurements, let

$$D = R_A + R_B - R_C - b$$

$$E = R_A^2 + R_B^2 - R_C^2$$

$$F = R_A^3 + R_B^3 - R_C^3$$

Also let

$$\begin{aligned} G &= \sum \frac{D^2}{R_C^2} & H &= \sum \frac{DE}{R_C^2} & J &= \sum \frac{DF}{R_C^2} \\ K &= \sum \frac{EF}{R_C^2} & L &= \sum \frac{E^2}{R_C^2} & M &= \sum \frac{F^2}{R_C^2} \end{aligned}$$

the summations being made over all the separate sets of measurements. The parameters are given by:

$$\tau = \frac{JK - HM}{LM - K^2} \quad \nu = \frac{HK - JL}{LM - K^2}$$

The derivation of this and other cases and illustrative applications are described in the original report (84). The computation is best carried out with the aid of a desk calculating machine.

This method is recommended for precise measurements of radioactivity. It extends the useful range of α -counters to the point where the correction is $\sim 10\%$ and of Geiger counters to that where it is well over 20%.

METHOD OF PROPORTIONAL SOURCES (87). This method does not require any assumed mathematical expression for the behavior of the instrument, but requires a set of radioactive sources of identical physical condition and of accurately known relative strengths. Each source is measured under identical conditions of geometry. This obvious method, or its equivalent, has been used or proposed many times, but no satisfactory method of working up the data has been described. One cannot, as is often done, base the absolute intensities on the measurement of the weakest source, for it is impossible to make its random and nonlinearity errors simultaneously insignificant.

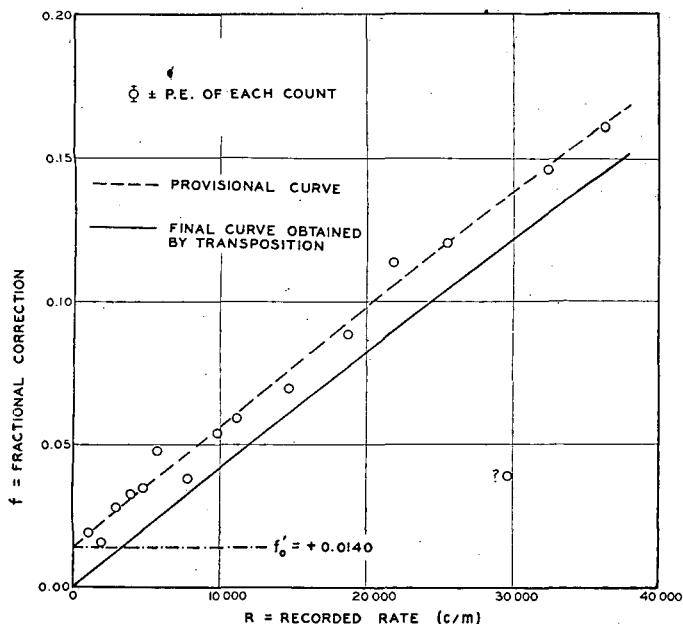


Figure 7. Determination of Nonlinearity Correction by Method of Proportional Sources

A + alcohol-filled self-quenched Geiger counter

If the relative strengths of sources $i, j, k \dots$ are given by $q_i, q_j, q_k \dots$, then there exists a factor A such that for each source:

$$N_i = q_i A + b$$

$$f_i = (N_i - R_i)/R_i = (q_i A + b - R_i)/R_i$$

The value of A will depend on a number of factors and cannot be known in advance. Instead, a provisional approximate value A' , is adopted from inspection of the data. Provisional fractional corrections are calculated for each source:

$$f'_i = (q_i A' + b - R_i)/R_i$$

A plot is made of f'_i against R_i , and the best smooth curve through the points is drawn. This curve should approach asymptotically a straight line as $R \rightarrow 0$. The intercept with the $R = 0$ axis will not, however, be at $f' = 0$ unless by chance $A' = A$. Designating the value of the intercept by f'_0 , the value of A can be obtained simply from:

$$A = A'/(1 + f'_0)$$

Now the calculations can be repeated, giving f as a function of R . The curve must now pass through the origin. However, a preferable procedure involves simple transposition of the provisional curve by use of the relationship

$$f = f' - (1 + f')f'_0/(1 + f'_0)$$

The new computations need only be made for a few selected values of R , using corresponding values of f' read off of the curve rather than those from the data.

An illustration of the application of this method to a Geiger counter is given in Figure 7.

The proportional sources were prepared by dilution by gravimetric aliquoting of a stock solution of RaDEF, prepared from spent radon tubes, and evaporating a definite volume of each solution, measured with a micropipet, onto a 2.4-cm. (1-inch) disk stamped from 0.2-mm. (0.008-inch) stainless steel sheet. Measurements were made under conditions such that only the more penetrating RaE β -rays were detected, and each was counted for a sufficient time to reduce the random probable error to 0.25%.

The calculations can be performed rapidly and to sufficient accuracy with a slide rule. An alternative procedure to that described, which requires a calculating machine, is to assume a relationship of type e and to calculate the necessary number of parameters (generally A, τ , and ν) by the method of least squares.

The preparation of proportional sources of sufficient accuracy is not easy, and not feasible in some laboratories. An alternative procedure would be to make the sources with only approximately predetermined strengths and to calibrate them by use of an instrument whose nonlinearity corrections have been accurately determined by another method, such as that of multiple paired sources, or by the use of a master set of proportional sources. The value of this method would be greatly enhanced if sets of calibrated proportional sources were readily available commercially or through a suitable agency. The problem of preparing and calibrating master sets for various types of instruments is being taken up with the National Bureau of Standards.

The method of radioactive decay may be regarded as a special case of this method. Here a sample of a radionuclide of convenient and accurately known half-life is measured at various times during its decay. The calculations can be made exactly as described above, using $q(R) = e^{-\lambda t}$, where λ is the decay constant and t is the time of measurement, measured from any reference point. Nuclides which have been used or should be suitable for this purpose are ThC (60.5 minutes half-life) (44), Rn (3.824 \pm 0.002 days) (34, 71), RaE (5.00 \pm 0.02 days), I¹²⁸ (24.99 \pm 0.02 minutes) (72), In¹¹⁶ (54.31 minutes) (99), and Mn⁵⁶ (2.59 hours). The former three are descendants of readily available natural radionuclides, and the latter three are produced by slow neutron reactions with large cross sections, and can be made easily in any laboratory having access to a source of neutrons.

Having determined the nonlinearity corrections for a given instrument, subsequent measurements with that instrument can be corrected (before subtraction of the background) by applica-

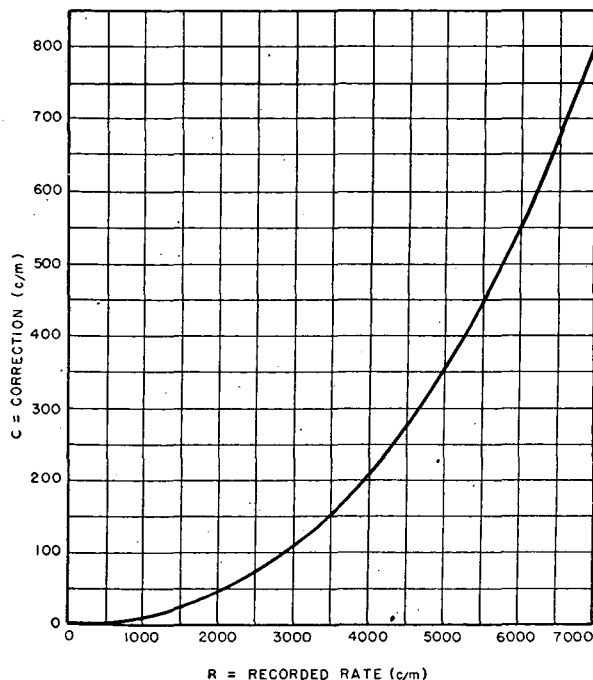


Figure 8. Nonlinearity Correction Curve, Linear Plot

Air-filled α -ionization counter

tion of the appropriate equation such as $a-e$ or plot such as Figure 7. For greater convenience in routine work, a plot of the correction $C = N - R$ as a function of R can be made and posted near the instrument. Figure 8 is a typical plot on a linear scale,

which is useful when the range of C and R values is not too great, and Figure 9 shows a log-log plot, which allows a large range of values to be included.

Inconstancy of Detector Sensitivity. A disturbing feature for accurate radioassays is the variation in sensitivity exhibited by Geiger counters in particular and by some other types of detectors as well. The organic vapors used for quenching the Geiger discharge become decomposed with usage, resulting in a gradual change in the voltage-response characteristic curve and an eventual loss of suitable counting characteristics. Slow leakage can have a similar effect. Similar inconstancies may arise in ionization counter amplifiers and electrometer circuits as a result of aging effects in vacuum tubes and resistors, replacement of circuit components, and temperature and humidity effects. Such variations can be detected and corrected for by the use of a normalization standard of constant activity. Statistical treatment of the standard measurements to distinguish true from random fluctuations has been described (74).

A normalization standard can also be used to intercompare measurements made with different instruments in the same laboratory. This is often necessitated by the replacement of a counter tube. In general, the ratio of sensitivities of two different instruments depends on the type and energy of radiation, and may be different for an activity of interest and the standard unless the latter is of the same radionuclide or has closely similar radiations.

In many applications of radiochemistry it can be arranged to make all measurements whose ratios are desired in a time so short that detector sensitivity variations are insignificant.

ABSOLUTE MEASUREMENTS

In ordinary tracer work a suitable unit of intensity is the apparent activity of an arbitrary standard or an instrumental unit such as count per minute or scale division per second. For many physical measurements and for therapeutic use of radioelements, absolute numbers of radiations or of disintegrations are required. The fundamental unit is the disintegration per second; special units are the curie = 3.70×10^{10} disintegrations per second (114, 134), and the rutherford = 10^6 disintegrations per second (24, 114).

Counting Yields. For the ratio of counts to disintegrations the expression counting yield [compare the German *Strahlungsausbeute* (132) and *Zählrohrausbeute* (35)] has been proposed (73). The counting yield is a function of the particular detector and arrangement used and the radiation characteristics of the nuclide being measured. Counting yields may be specified for radiations as well as for disintegrations. The counting yield of a nuclide emitting more than one radiation is the sum of the counting yields of the separate radiations, each multiplied by the average number of times it occurs per disintegration. For a specific single radiation, the counting yield, y , may conveniently be regarded as the product of geometry factor g , absorption factor a , self-absorption factor s , back scattering factor b , and detector efficiency e :

$$y = g \times a \times s \times b \times e$$

The various factors are not strictly independent of each other, and others are occasionally added.

GEOMETRY FACTOR. The geometry factor is defined as the fraction of the particles emitted in the source in the direction of the aperture or sensitive volume of the detector. (The term geometry is used in this paper to express the entire arrangement of sample and detector.) Some arrangements permit easy calculation of the geometry factor, especially when the radiation is selected by a sharply defined aperture at a definite distance from a well defined source (49, 73, 88, 132, 159). This condition is met in some "low-geometry" α -counters designed for this purpose. Similar calculations can be made for the commonly used end-window Geiger counter, in which the anode terminates in a bead a few millimeters from the window, if the sensitive volume is assumed to begin at approximately the point of contact of the wire with the bead (159). In counters in which the activity is spread on a plane surface inside the sensitive volume, the geom-

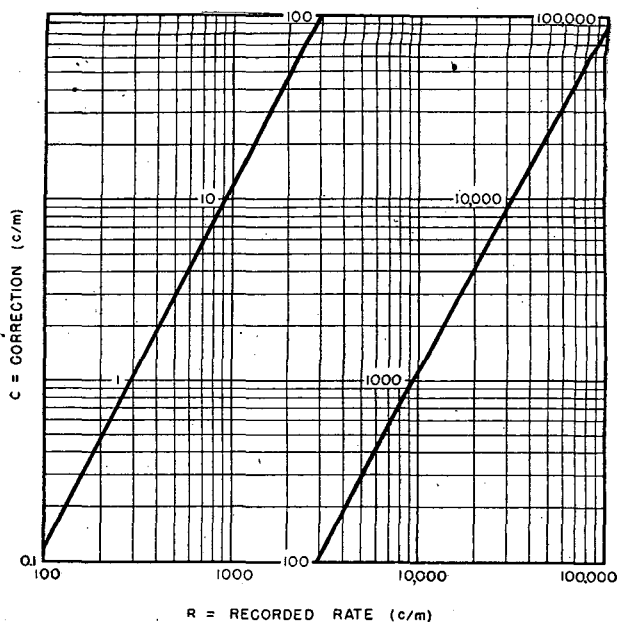


Figure 9. Nonlinearity Correction Curve, Log-Log Plot

H₂-filled externally quenched Geiger counter

etry factor is regarded as one half. With complicated or poorly defined arrangements, however, the geometry factor is not easily calculable, and is generally estimated from the counting yield, as determined by means of a source of known absolute strength, and estimates of the other factors.

ABSORPTION FACTOR. When different from unity because of the presence of material between the source and the detector, the absorption factor may be estimated by adding absorbers in increments and extrapolating the resulting absorption curve back to zero total absorber. For a given source, the slope and shape of the absorption curve depend on the atomic number of the absorber and its disposition relative to the source and detector. In some cases, particularly with absorber close to a source of β -radiation, the "absorption curve" exhibits an initial rise instead of a fall, resulting from an excess of "in-scattering" over "out-scattering." Consequently, in determining the effect of an absorbing layer, the absorbers should be in as nearly the same position and of the same atomic number as the material in question, and separate absorption curves should be taken to correct for the counter window and any material directly covering the source. In a special study of this type, the effect of the air between the sample and detector was estimated by inserting thin films of plastic at various positions (159).

SELF-ABSORPTION FACTOR. Estimated as described above.

BACK-SCATTERING FACTOR. Back-scattering can be eliminated by use of essentially weightless sources mounted on extremely thin films. Back-scattering factors can then be estimated by placing layers of material close behind the sources. The backing material is "infinitely thick" when its thickness exceeds half of the effective range of the radiations. For β -radiation, the saturation back-scattering factor increases with atomic number of the scatterer and depends also on energy, window thickness, and other conditions of measurement. Factors as high as 1.5 to 1.8 have been reported (69, 154, 153, 159). In the case of α -particles, two essentially different modes of scattering occur, small-angle multiple scattering and large-angle single scattering. The former is important in parallel-plate geometries, leading to factors as high as 1.05 for thin samples on platinum (28, 119). Under conditions of low geometry only single scattering is important, but probably contributes less than 0.1% to the observed intensity.

EFFICIENCY OF COUNTER. The term efficiency is here used for the ratio of counts (after correction for nonlinearity and background) to incident particles. It is close to unity for most common α - and β -counters. The variations of Geiger counter sensitivities may be regarded as variations in efficiency; the apparent efficiency may be greater than unity when multiple discharges are present. Geiger counters operating at low gas density, electron multiplier tubes, crystal counters, and scintillation counters generally have efficiencies below unity. Gamma-ray counter

efficiencies (17, 19, 35, 37, 102, 103, 116, 126, 127) are low and depend on the energy and the material of construction. Brass-wall counters of ordinary size have efficiencies of roughly 0.01 times the γ -energy in million electron volts in the range 0.3 to 3 m.e.v.

Determination of Disintegration Rates. Absolute disintegration rates of samples of some nuclides can be determined by estimation of the counting yield by the methods just described. For accurate measurements counting arrangements must be specially designed to eliminate as much as possible scattering and absorption effects; their estimation is subject to error, particularly when long extrapolations must be made. The use of evacuated collimating tubes is standard for α -radiators, and has been applied to a lesser extent for β -emitters (31). Moderately accurate determinations of β -disintegration rates can be made by careful work with standard end-window counter tubes (159, 160). Counting of active gases may be adapted to this purpose under conditions such that every disintegration in the sensitive volume of the counter gives a discharge (4, 97). In some cases where the disintegrating atom emits more than one radiation simultaneously, coincidence counting techniques can give the absolute disintegration rate (37). Combination of calorimetric measurements with a knowledge of the radiation spectrum has also been used (160). Finally, genetic relationships may be used for nuclides that have a radioactive ancestor or descendent whose disintegration rate can be more easily determined.

Radioactive Standards. Absolute measurements in a given laboratory may frequently be reduced to relative measurements by the use of absolute standards prepared elsewhere by methods such as those described. Alpha-ray standards are generally unnecessary because of the accuracy with which counting yields can be calculated. Pu²³⁹, because of its long lifetime and the relative stability of its immediate decay product, has proved excellent as an α -ray standard. Po²¹⁰ in transient equilibrium with RaD is of greater practical importance because of its unrestricted availability. UX and RaE are useful β -ray standards because of their genetic relationships to α -emitters, U²³⁸ and Po²¹⁰, respectively. Radium has for many years been the standard of

γ -radiation, but is unsatisfactory because of the complexity of the γ -radiation associated with it. Co⁶⁰ is proving more satisfactory.

A nationwide program for the preparation and calibration of absolute standards of many of the nuclides which are important for isotope work and radioelement therapy is under way. Beta and gamma standards of Co⁶⁰ are available and standards of I¹³¹, C¹⁴, P³², and Na²² are being developed (30, 113).

STATISTICAL CONSIDERATIONS IN RADIOACTIVITY MEASUREMENT

Statistics of Counting. The laws of random events as expressed by the Poisson distribution and the corresponding Gaussian approximation, and their application to the counting of radioactive particles, are well known (see, for example, 74, 142). More complicated distributions encountered with rapidly decaying sources and in some cases of genetically related activities rarely need to be considered in measurements in applied radioactivity. This permits a simple and straightforward calculation of the uncertainty of counts and counting rates.

Statistics of Ionization Chamber Measurements. The statistical laws governing the behavior of current- and charge-type ionization chambers are complicated by the variability of the ionization per particle; moreover, the distribution of ionization is generally unknown. Approximate treatments based on simplified assumptions regarding this distribution have been given (42), but in practice the precision is generally determined by repeating each measurement several times and calculating the standard or probable error by standard statistical formulas. Instruments of this type are most often used for radiation levels sufficiently high that random fluctuations are relatively small and may often be disregarded. When the fluctuations are so large as to be important, it is often advisable to substitute a counter for the measurement.

Combination of Random Errors. In general, a desired result is obtained by combining two or more measurements, each of which possesses an uncertainty.

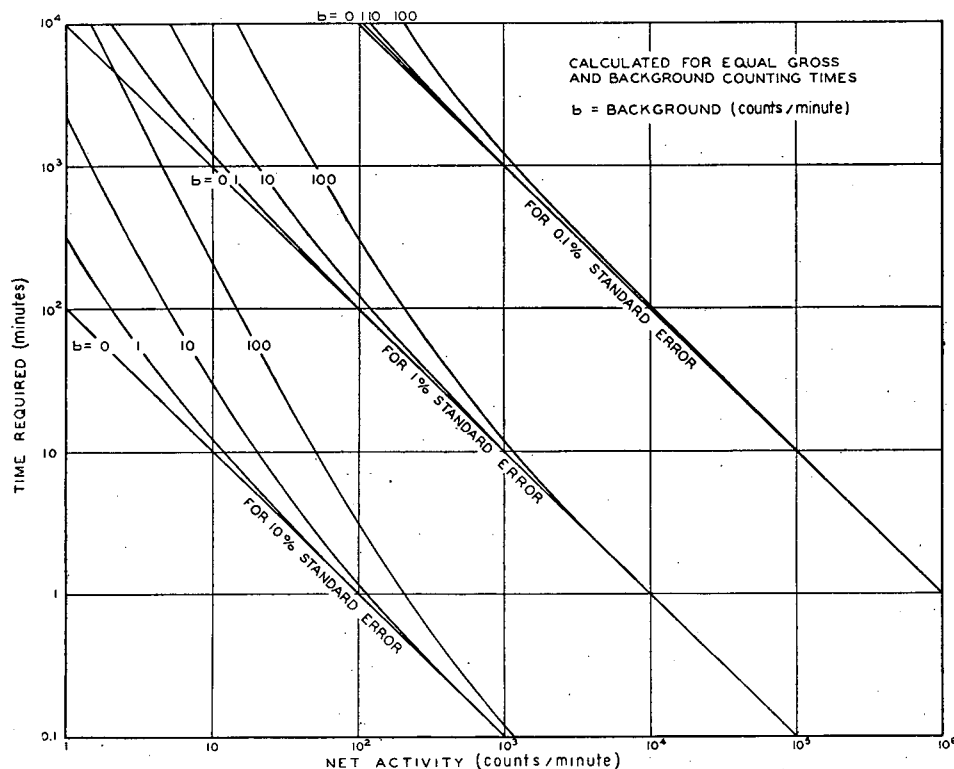


Figure 10. Effect of Background on Required Counting Time

The precision index, f , of a result, F , which is a function of quantities A, B, \dots having precision indexes a, b, \dots is calculated by the well-known law of propagation of errors:

$$f = \left[\left(a \frac{\partial F}{\partial A} \right)^2 + \left(b \frac{\partial F}{\partial B} \right)^2 + \dots \right]^{1/2}$$

Thus, in some specific cases of interest:

$$F = A \pm B \pm \dots \quad f = (a^2 + b^2 + \dots)^{1/2}$$

$$F = A \times B \times \dots \quad f =$$

$$F \left[\left(\frac{a}{A} \right)^2 + \left(\frac{b}{B} \right)^2 + \dots \right]^{1/2}$$

$$F = \frac{A}{B} \quad f = F \left[\left(\frac{a}{A} \right)^2 + \left(\frac{b}{B} \right)^2 \right]^{1/2}$$

$$F = A^n \quad f = naA^{n-1}$$

The first of these is applicable to the determination of the net activity by subtraction of the background, and the third to ratios of activities.

Planning of Experiments and Measurements. Statistical

considerations are valuable as a guide in the planning of radiochemical experiments in order to obtain a desired precision in the final result and to economize time and radioactive materials. A conclusion already mentioned is that instrumental backgrounds should be made as low as possible. This is particularly important when weak activities must be measured; Figure 10 illustrates the effect of the background (assumed constant) on the time necessary to obtain a given precision in the net result. Where possible, sufficient activity should be used to give an effect several times the instrumental background level in each sample measured. Time should not be wasted in making any measurement to a degree of precision much greater than that of other measurements with which it is to be compared or combined. (An exception to this rule involves the background; more extensive measurements of this than are indicated by the conclusions of statistical reasoning alone serve a useful purpose in checking the behavior of the instrument and detecting contamination.)

An example of an application of statistical principles is illustrated by Figure 11. It is routine practice in many laboratories to count all samples until a certain predetermined number of counts has been accumulated. In this manner the relative uncertainty of each gross measurement has the same value. However, because of the effect of the background, the relative uncertainty in the net result depends on the activity level. When a large fraction of the total counts comes from the background, the precision of the net result is considerably reduced. To obtain the same precision for weak as for active samples, the total number of counts must be increased, and hence the counting time prolonged. Figure 11 gives the total number of counts which must be accumulated for a definite net precision as a function of the counting time required for this accumulation. A plot of this type is used by continuing each count until the point defined by the number of 4 accumulated counts and the elapsed time crosses the curve.

Accidental Variations and Errors. Random errors and uncertainties arising from other sources than the randomness of radioactive disintegration and cosmic rays are generally present and frequently important in radiochemical work. These may arise from variations in chemical analytical techniques or in the preparation and mounting of the sample. They may also result from variations inherent in the process under investigation, particularly if it is of a biological nature. Standard statistical methods appropriate to the particular problem itself should, of course, be used in all cases.

CONCLUSION

Like analytical methods in general, radioactivity measurement is subject to considerable variation in precision. The accuracy of radioassays has never equaled that of the best analytical methods, but is comparable to that of many in common use.

Instrumental errors and uncertainties can generally be reduced to about 1%, and in some cases to about 0.1%, by application of properly determined corrections. Unfortunately, the inconsistency of most Geiger counter sensitivities makes difficult greater precision than about 1% when used for the measurement of β -activity. Gas-flow proportional counters used for β -activity are claimed to have high inherent stability (5, 18). It is not clear whether the use of internal samples takes maximum advantage of this stability. Greater accuracy might possibly be obtained with such counters equipped with thin windows to permit the use of external samples (5).

Sample errors are generally larger than instrumental, although measurements of α -activity with low-geometry counters are with care capable of reproducibility to about one part per thousand. The best routine sample preparation techniques for β -emitters give reproducibility only to the extent of 1 to 3%. Some of the crude techniques often used introduce uncertainties of 10 to 50%.

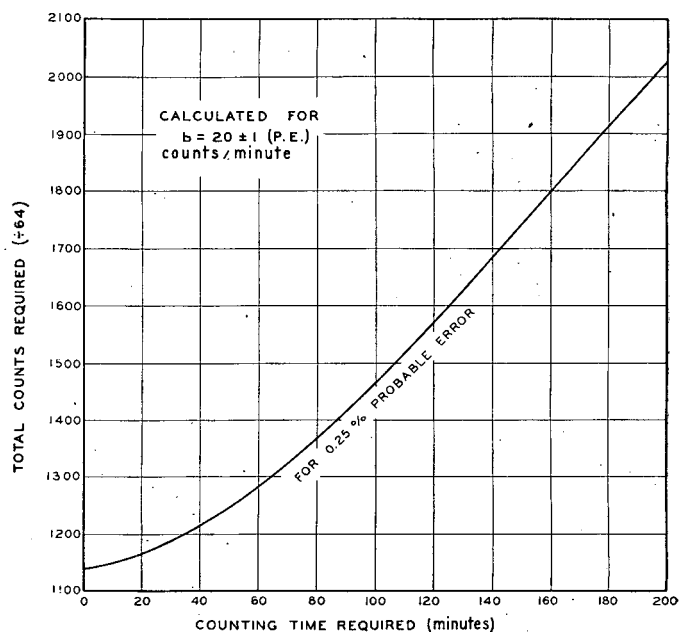


Figure 11. Total Counts Required vs. Time Required

For given relative error in net counting rate

It is to be hoped that the development and improvement of convenient and highly reproducible methods of sample preparation will be extended to all the important radioactive elements and compounds, so that sample errors will no longer be the limiting factor.

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Industrial Applications of Radionuclides

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Radionuclides are used as labels of atomic dimensions by which molecules can be indelibly marked, and as high-energy sources of radiation. Like other research tools, radionuclides have moved rapidly from the laboratories of basic research to applied research and are now going into engineering applications. Examples of industrial applications are cited and problems discussed.

RADIONUCLIDES have contributed two important tools to the bulging work kit of the man of research. These research tools, like others in the past, have moved rapidly from the laboratories of basic research to applied research and are now moving into engineering applications.

The first and most important tool is a tag or label of atomic dimensions with which molecules can be indelibly marked. This marking provides a means of analysis of unsurpassed sensitivity and specificity. The second tool is a high energy source or radiation that is small and readily portable, and requires no external supply of power.

TRACER USES

A more detailed consideration of uses of radionuclides permits a breakdown of tracer uses into two categories: chemical tracing and physical tracing. In chemical tracing it is necessary to use radioisotopes of the element whose chemistry is to be studied. The element, containing its radioisotope, is synthesized into the desired form of ion or molecule or is prepared in its elementary form, pure or alloyed. This material is then added to the system of interest and the labeled material is followed through all the chemical and physical changes occurring in the system, with the assurance that the behavior of the radioisotope truly reflects the behavior of the labeled element.

An example of this type of tracing is a study of the distribution of phosphorus between slag and steel. Calcium phosphate containing P^{32} is synthesized and added to the slag. The rate of appearance of P^{32} in the steel is a measure of the rate at which phosphorus reaches equilibrium between the two phases (Figure 1). Combined with a chemical analysis for total phosphorus,

the value of the equilibrium constant can be obtained. The factors controlling rate and equilibrium can be investigated by appropriate variations of temperature, calcium-phosphorus ratio, etc. (24).

Physical tracing or the tracing of mass transfer of material can be carried out by introducing a radioisotope of any element present in the system. In these studies, however, greater latitude in the choice of radionuclide is possible. If no chemical reaction or change of phase of the component of interest occurs, any radionuclide of suitable characteristics can be introduced. Because the analytical methods used are very sensitive, the concentration of foreign material can be made so small that it will not materially affect the properties of the system.

An example of physical tracing is the use of radiomanganese to measure the distribution of DDT on the ground when sprayed from low flying airplanes. Here an oil-soluble compound of manganese (Mn^{52}) was chosen because of its favorable radiation characteristics and half-life) is dissolved in the standard DDT formulation. Samples taken from the sprayed area are analyzed for radioactivity, which is proportional to the DDT present. Quantities of DDT as small as 10 grams per acre are readily measured. Dyes and other additives can be used in the same manner, but the ease of analysis and high analytical sensitivity favor the use of radioassay methods. Because the oil solvent is volatile, this type of tracing could not be used to study the behavior of the oil in such spraying operations. Separation of the tracer and material to be studied must not occur.

USE AS RADIATION SOURCE

In tracer work the emphasis is on the material emitting radiation, and the radiation itself is used for measurement only. In

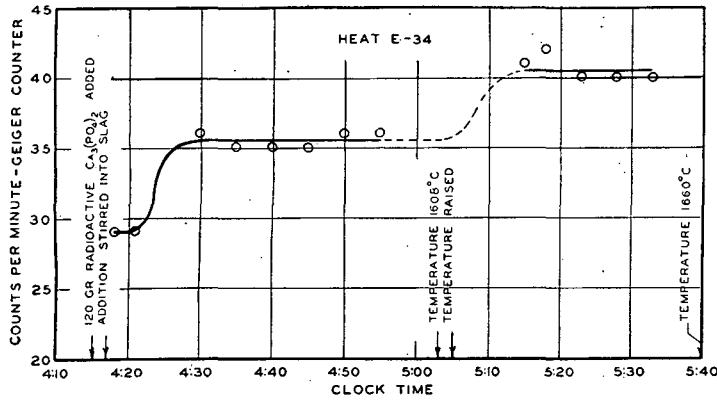


Figure 1. Distribution of Phosphorus between Slag and Steel (24)
Rate at which phosphorus reaches an equilibrium distribution between two phases is readily determined. Effect of temperature on equilibrium is also shown

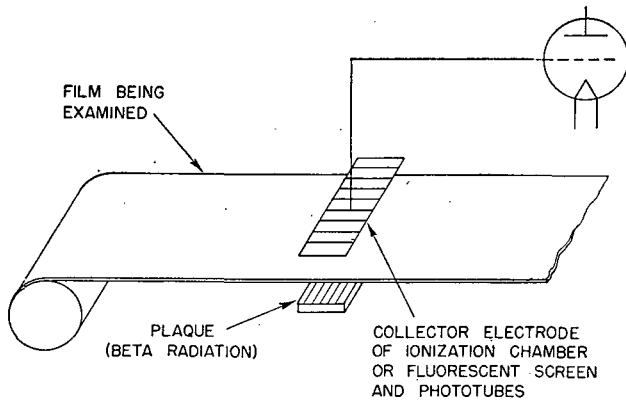


Figure 2. Schematic Diagram of Thickness Gage for Thin Film (2)

Radiation source can be an α -, β -, or γ -ray emitter to suit nature of film being measured

the use of radionuclides as radiation sources this emphasis is reversed. Here the material is relatively unimportant but the radiation and its effects are of paramount interest.

Two different points of view are reflected in the use of these radiation sources. In one case the effects of the radiation on matter are important. Radiations from radionuclides produce ionization in any material through which they pass. This ionization has been useful for the removal of electrostatic charges that accumulate on moving insulators, such as cloth and paper, during their manufacture (2). If the air adjacent to moving material is ionized, static charges can leak off, thus preventing sparking. Dust and vapor explosions due to such sparking can be eliminated in this way.

The other viewpoint for considering radiation sources is the effect of matter on the radiation rather than the effect of radiation on matter. Advantage is taken of this viewpoint in determining the attenuation of a beam of radiation by placing absorbing material between the source and a detector. Because the attenuation of the beam of radiation is a function of the absorber, the degree of attenuation can be made a measure of thickness. A thickness gage for plastic film has been developed on this principle (5). As there is no physical contact with the material being measured; soft plastics can be measured accurately without consideration of deformation in the actual measuring process (Figure 2). The method also permits measurement of moving films, and can therefore be used for process control as well as analysis.

Before numerous examples of industrial applications of radionuclides are discussed, it is well to consider just what is meant by

industrial application. As used here it denotes the use of radionuclides for investigations or developments whose immediate objective is the creation, improvement, or control of industrial processes or products. Any investigation leading to a better understanding of an industrial process would also be included for out of such understanding will come eventual improvement.

EXAMPLES OF INDUSTRIAL APPLICATIONS

As Tracers. The following examples of industrial applications of radionuclides are considered as product and process research, both in the laboratory and in the plant, and product and process control. Much has been written on proposed uses, a moderate amount of information is available on work in progress, but very little has been published on completed work. The examples discussed below are taken from the last two categories in order to minimize the speculative element. An idea of the present state of industrial uses can be gained

from recently published information from the Atomic Energy Commission (1). In the last two years 3136 shipments of radionuclides have been made by the Isotopes Division at Oak Ridge. Of these, 90, or 2.9% have been allocated for industrial research.

Probably the largest scale experiment on an industrial process was recently completed by one of the steel companies and its consultants (7, 16).

One of the important sources of undesired sulfur in steel is the coke used in the blast furnace. Because sulfur in coal is mainly in two forms, pyritic and organic, and the ratio of these two forms varies in different coals, it was desirable to know which type of sulfur in the coal was carried over into coke. If one form was preferentially eliminated in the coking process it would be possible to exercise some control over the product by judicious choice of starting material. Because the conditions existing in a coke oven cannot be readily duplicated in the laboratory, a full scale plant test was necessary.

Pyrites containing S^{35} were synthesized in the laboratory and then intimately mixed with 12 tons of coal. This represented a single charge in the coke oven. During the coking operation gas evolution was carefully measured and the total and radioactive sulfur content of the gas was determined at regular intervals. After the coke had been discharged, representative samples of the product were also analyzed for total and radioactive sulfur. The results showed that the ratio of radioactive (pyritic) sulfur to total sulfur was the same in both gas and coke and was equal to the ratio of pyritic to total sulfur in the original coal. This is interpreted as meaning that all the sulfur in coal is equivalent in the coking process and that the ratio of pyritic to organic sulfur in the coal does not influence the sulfur content of the finished coke (Figure 3).

An extensive series of laboratory studies is being made by oil companies. The mechanism of reactions occurring in petroleum processing naturally occupies the spotlight (10). Catalytic cracking and the Fischer-Tropsch synthesis are being attacked from many angles. Studies on the flow of the three-phase system, oil, water, and gas, through porous media, should lead to a better understanding of some of the problems connected with petroleum production (1).

The mechanism of friction and the role of lubricants in friction are also being studied (4, 12, 20, 21). It has been demonstrated that when two metal surfaces rub against each other metal is transferred from one surface to the other. By making one surface radioactive, the quantity of material transferred can be measured even when the surfaces are made of the same metal and are extremely hard; as with chromium plate or nitrided steel (Figure 4). When the bearing surfaces are lubricated the metal transfer is reduced but not eliminated. Information has also been obtained on the role of addition agents in lubricants (6).

Lubricants are used on textile materials as well as on metals to aid in the spinning and weaving processes.

In one case a rayon manufacturer wanted to measure the distribution of lubricant on rayon yarn. Difficulties encountered in

spinning and dyeing made questionable the uniformity of distribution of the lubricating finish and an attempt was made to measure the distribution. As the finish contained sodium oleate, radiosodium was introduced into the finish as this compound. Treatment of the yarn was carried out on a laboratory scale and the radiosodium measured on samples as small as 1 cm. long. As the yarn was 150 denier (150 grams per 9000 meters), these samples weighed only about 0.2 mg. and each sample contained about 0.04 microgram of sodium (Figure 5). In the laboratory test a high degree of uniformity was indicated by the sodium distribution, but because this was a "physical tracer" it was not possible to determine whether or not the other components of the lubricant were also uniformly distributed. However, these tests do show the extremely high sensitivity of the analytical method.

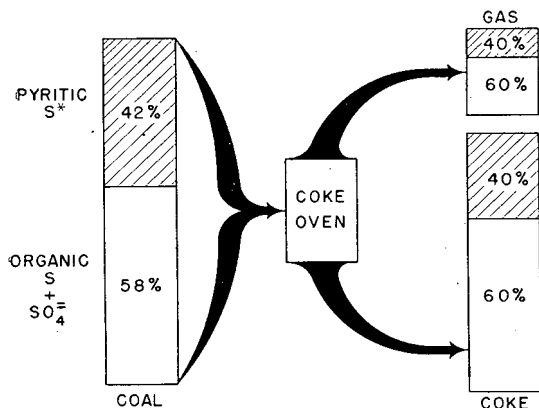


Figure 3. Schematic Diagram of Behavior of Sulfur in a Coking Operation

Pyritic sulfur (S*) labeled with S³² tracer

A similar study on measurement of the amount of ink laid down in printing has been published (3). A small amount of the varnish used in the ink was phosphorylated with phosphorus pentachloride containing P³², and mixed in a suitable batch of ink and the printing was carried out. Direct β -ray measurement on the product gave a measure of the amount of ink deposited. From such measurements variations in the quality of printing can be related to the quantity of ink involved. Other variables such as paper quality and printing temperature can also be studied.

Some other uses for radionuclides in process development have been mentioned briefly in the literature but no results reported. Radiosulfur is being used to study the mechanism of rubber vulcanization and the action of modifiers in GR-S production. Radiophosphorus is being used to study the diffusion rate of plasticizers in plastics and the amount and location of phosphorus in steel (1). Radiocarbon and a number of metals are being used in metallurgical and ore processing studies (14, 15, 23).

Radionuclides are also playing a role in product development.

A manufacturer of salt blocks for animal feeding wished to test the efficacy of various compounds to be added as mineral supplements (17). It was desired to balance water solubility against utilization by animals. If too soluble the additives would be leached out readily and if too insoluble they would not be utilized effectively. Radioiodine, radiocopper, and radioiron in various forms were fed to experimental animals. Urine, feces, and blood were analyzed for radioactivity at intervals and excretion rates were determined. In this way it was determined that dithymol diiodide was a suitable form for incorporating iodine but that ferric phosphate was not sufficiently soluble to be utilized by the animals. As a result of such tests a suitable compound was selected for each of the supplemental elements added to the salt cake.

The fields of biology and medicine furnish numerous examples of this type of product development. Frequently such work is done at a very fundamental level, yielding results of much greater value than mere product improvement (18, 19).

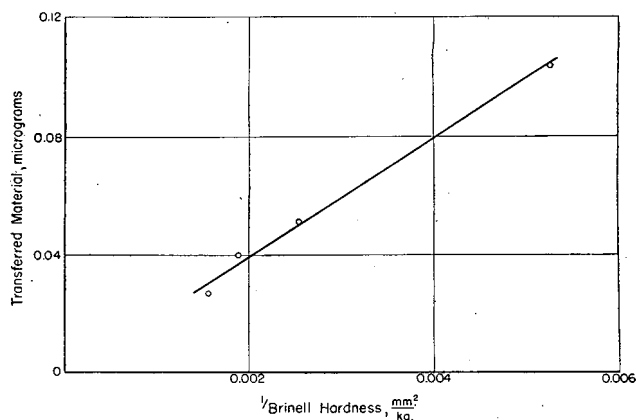


Figure 4. Transfer of Beryllium-Copper to a Steel Ball as a Function of Beryllium-Copper Hardness (20).

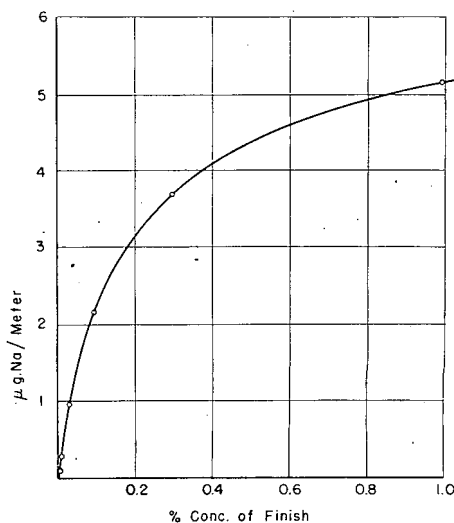


Figure 5. Weight of Sodium on Rayon Yarn as Function of Finish Concentration in Treating Bath

Radiosodium added to finish bath in form of sodium oleate

Another application of tracers to what might be called process control is found in the accumulation of evidence for legal action.

One such case involved a death where mercury poisoning was suspected (11). The girl had worked in a fluorescent lamp plant where she tubulated lamps in preparation for pumping. The tubulation contained a small droplet of mercury. It was necessary to know how much mercury vapor could be inhaled in the sealing operation. Using radioactive mercury in a test setup it was found that the average concentration of mercury vapor in the air in the tubulation equipment was 0.01 mg. per cubic meter which is 10% of the accepted safe limit. These measurements involved weights of mercury as small as 10⁻⁸ gram.

Radionuclides have also been used to trace water flow in cases involving stream pollution (10).

Other tracer applications could be mentioned, but this field is so new that published results are still meager.

As Radiation Sources. The use of radionuclides as sources of radiation is increasing. Before the advent of pile-produced radionuclides radium was by far the most important element in this field and it is still most widely used. Applications based on ionization produced by the radiation have been mentioned in connection with static charge elimination. Luminous paint for watch and instrument dials depends upon ionization produced in fluorescent compounds. A less well-known application is the

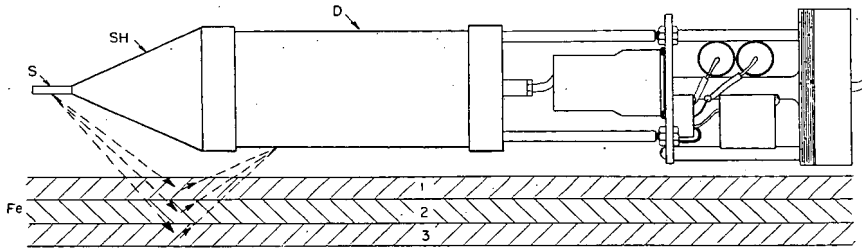


Figure 6. Schematic Diagram of Penetron Used for Measuring Pipe Thickness (8)

S. γ -ray source such as radium. SH. Lead shield to protect ionization chamber, D, from direct radiation from source

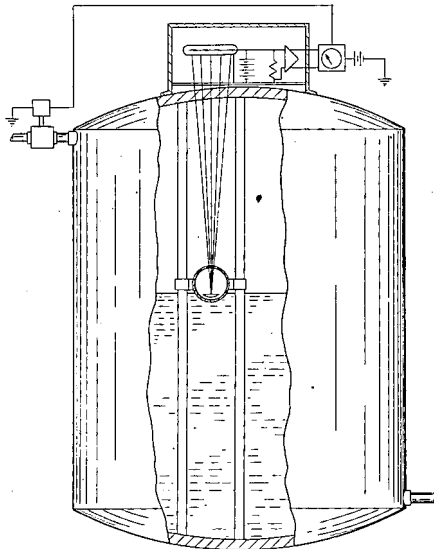


Figure 7. Float-Type Liquid Level Indicator (22)

γ -ray source such as radium or Co^{60} is sealed in hollow float in tank. Radiation is detected with counter or ionization chamber on top of tank. Output of detector actuates input valve controlling liquid level

use of radionuclides to provide an ever-present source of ions in gas discharge devices. Certain types of radar equipment require gas discharge tubes that will respond to an applied potential within fractions of a microsecond. In the absence of ions in the gas the discharge may be delayed a thousandfold or more. However, if a small amount of radium or Co^{60} is provided in the tube, ions are always present and rapid reliable discharge characteristics are obtained. Some work has been done to develop this technique for fluorescent light "starters."

The other general use of radiation sources depends on the effect that material or distance has on the amount of radiation reaching the detector. Radiography of large castings falls into the category. Radium, radon, and Co^{60} have found considerable use in this field (18). Flaws in the casting are shown on the photographic film, owing to a smaller absorption of the radiation in the flaw and consequent greater darkening of the film. The thickness gage mentioned above also operates on the principle of varying absorption of radiation. In this case electronic rather than photographic detection is utilized.

Another type of thickness gage depends on scattered rather than transmitted radiation.

This device is available commercially and is used to measure thickness of pipe and plate where only one side of the object is accessible (8). For a given material such as iron or steel the output of the instrument can be calibrated directly in units of thickness. It will measure pipe up to 1.25 cm. (0.5 inch) thick

with 5% accuracy (Figure 6). This instrument can also measure thickness by transmitted radiation but is less sensitive for thin sections than the first one mentioned. The instrument is used extensively in the petroleum industry.

Utilizing this principle of measuring scattered radiation, the density of solutions in a tank or flowing in a pipe can be measured, and the location of liquid-liquid or liquid-gas interfaces can be accomplished. Because the output of the instrument is electrical it can be readily adapted to process

control by actuating valves regulating the flow or the dilution of reagents.

Another type of liquid level indicator operates on the principle that the measured intensity of radiation from a small source changes as the inverse square of the distance between the source and detector (Figure 7). By having a source on a float and the detector at the top of the tank, liquid level is readily measured (22). Any long-lived γ -ray emitter can be used with these instruments.

The area of small irregular sheets of material can be measured by placing the object over a uniform plane source of radiation and measuring the decrease in ionization produced (2) (Figure 8). In this case polonium is used as a source of radiation, as its α -rays are completely absorbed by very thin sections of material (approximately 0.025 mm., 0.001 inch.)

An ingenious method of increasing the sensitivity of a semi-microbalance can be determined, so microgram quantities can be determined. A source of α -activity is placed on the end of the balance beam, so it sees a double ionization chamber. Displacement from the rest position is indicated by a meter connected with the ionization chamber (9) (Figure 9).

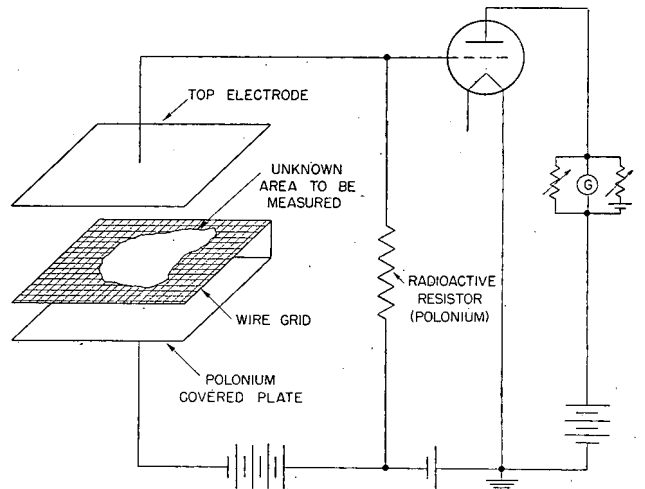


Figure 8. Schematic Diagram of Radioactive Area-Measuring Device (2)

PROBLEMS CREATED

In so far as use in industrial laboratories and use as sealed sources of radiation are concerned, the problems are known and their solutions are understood. Radiation hazard to personnel is the major problem here. However, the people using these materials are supposed to be familiar with these hazards and to know how to avoid them.

When the experimental work is taken out into the plant for large scale tests many additional problems arise. Scaling up the size of operations means scaling up the amount of activity needed.

This can very quickly reach levels so hazardous that the work is difficult to carry out with safety. Moreover, in plant tests the personnel does not have training in handling radioactive materials and proper supervision becomes increasingly difficult.

If the radioactive material is introduced into the plant product the problem of disposal becomes very serious. In most cases it is inadvisable to release a product containing radioactivity. If the dilution is great enough, the health hazard may be negligible but radioactive contamination of consumer goods must be avoided. In scientific laboratories such contamination could cause very serious trouble.

A situation of this type arose during the war when aircraft instrument wrappings were contaminated with radium-containing luminous paint. This paper was collected as waste, processed into cardboard, and made into boxes. When these boxes were used for packaging photographic film tens of thousands of dollars worth of critically short material was ruined. Many man-hours of labor were diverted to tracing down the trouble and a large expense was incurred to eliminate it.

A similar crisis was narrowly escaped after the war when surplus aircraft dials were sold for scrap brass and aluminum. Sufficient radium would have been introduced into the recovered metal to contaminate seriously all the brass and aluminum in the country.

Two uses of radionuclides suggested by poorly informed writers illustrate problems of personnel hazards and product contamination:

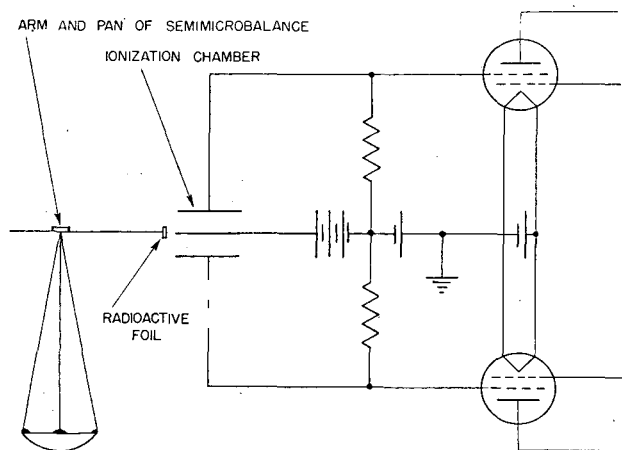


Figure 9. Schematic Diagram of Radioactive Microbalance (2)

The first involves adding radioactivity to toxic substances for monitoring air contamination. Because chemical poisons generally exist at very low levels of concentration, very high specific activity must be used to achieve the necessary sensitivity of detection. On any plant scale of operation this would involve prohibitive activity levels (Figure 10).

The second suggestion is to monitor the thickness of the tin continuously in tin plate or enamel in porcelain enamel. Radium or a radioactive isotope of some enamel constituent would be introduced and with the proper measuring equipment the amount of surface coating could be readily determined on the production line. In addition to sizable amounts of activity needed, with their accompanying hazards, the product would be contaminated. If a moderately long-lived nuclide were used the product would have to be stored for an unreasonably long period for the activity to decay. If a short-lived activity were used availability, cost, and greater difficulty of monitoring would decrease the desirability of the method.

In addition to the measurable disadvantages of having radioactivity in consumer goods, there is the imponderable factor of consumer psychology. Because of public ignorance of the

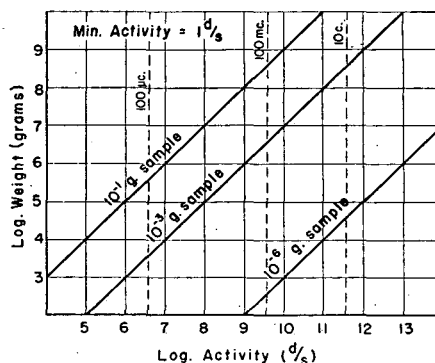


Figure 10. Amount of Radioactivity Needed to Label a System as a Function of Weight of System and Weight of Sample Measured

Calculated on basis of a detector capable of measuring minimum activity of 1 d/s in sample. Dotted lines show 100 μ c level, below which there is little danger of handling. From 100 μ c to 100 mc, simple precautions will allow for safe handling. In range of 100 mc. to 10 curies extreme care must be exercised in handling radioactive material. Above 10-curie level only special laboratories are equipped to handle such activities

hazards involved with radioactivity there is a very strong reaction of fear when radioactivity is mentioned. This has been fostered by inaccurately written stories in the newspapers and magazines and has been greatly augmented by scare-head statements by some of the scientific "authorities" in the field. Although the real dangers are negligible in any reasonable application, this distorted public viewpoint must be taken into account by any manufacturer using radioactive materials in his product.

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Phenyl- and Cyclohexyleicosanes

Infrared Absorption Spectra

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The infrared absorption spectra of 1-, 2-, 3-, 4-, 5-, 7-, and 9-phenyleicosane and of the corresponding cyclohexyleicosanes have been investigated between 1.5 and 15 μ . Per cent transmittance curves for two cell thicknesses are given as well as tables of wave lengths, wave numbers, and rough intensity estimates of the absorption maxima observed. A number of the absorption bands are associated empirically with vibrations of the phenyl ring, the cyclohexyl group, or the normal paraffin chain. A detailed comparison is made between the spectra of individual members of either series of compounds.

THE infrared absorption spectrum of a chemical compound is determined, approximately, by the masses and the equilibrium configuration of the atoms in a molecule, the energy required to give the molecule an arbitrary small deformation, and the change in the electric dipole moment produced by such a deformation. If the compound is composed of very simple or highly symmetrical molecules a complete interpretation of the infrared spectrum may be possible, and thus the potential energy function for the molecule may be determined. However, the molecules of the vast majority of compounds contain so many atoms that a detailed interpretation of the vibration spectra is at present out of the question. Nevertheless, by comparing the spectra of series of related compounds it is usually possible to trace certain relationships between the infrared spectrum and the structural formula. Such empirical correlations may be of great value to the analytical chemist.

In the present paper the infrared absorption in the 1.5 to 15 μ range of seven isomeric phenyl derivatives of *n*-eicosane and of the corresponding cyclohexyleicosanes is reported. The observed spectra are carefully compared with one another and with the spectra of related compounds, and a number of empirical relationships are established.

MATERIALS

The compounds investigated—1-, 2-, 3-, 4-, 5-, 7-, and 9-phenyleicosane and the corresponding cyclohexyleicosanes—were synthesized and purified at the Pennsylvania State College under American Petroleum Institute Research Project 42 (1, 2, 4, 5). The advisory committee for this project has specified a minimum purity of 95 mole %. The compounds are believed to be considerably purer, but no definite information about their purity is available.

EXPERIMENTAL

The spectrometer used is similar to one described by Wright (6). The optical parts include straight entrance and exit slits, a 60° rock salt prism of faces 8 by 10 cm., a collimating on-axis parabolic mirror of focal length 91.4 cm. and diameter 15 cm., and a plane Littrow mirror. The radiation emerging from the exit slit is focused by an elliptic mirror (foci at 7.5 and 37.5 cm.) upon a compensated two-junction vacuum thermocouple. The electromotive force generated is applied to a taut-suspension galvanometer, of period 1.5 seconds and sensitivity 1.25 microvolts per mm., and the deflection is amplified by a balanced barrier-layer photocell device. The deflection of the secondary galvanometer is recorded on 15-cm. (6-inch) bromide paper wrapped around a drum whose motion is synchronized with that of the Littrow mirror. The instrument will resolve 2 cm.⁻¹ at 14 μ , 2.5 cm.⁻¹ at 10 μ , and 4 cm.⁻¹ at 5 μ .

A Nernst glower operated on a voltage-stabilized 220 volt alternating current circuit served as source. The construction of the cells used has been described by Smith and Miller (3). Cells

of two thicknesses, 0.33 and 0.04 (or 0.06) mm., were used over most of the spectral range. The regions of strongest absorption were recorded also with a cell of thickness 0.012 or 0.015 mm. No attempt was made to measure the cell thicknesses with great accuracy. The cells of intermediate thickness were used in much other work during the 2 years the present investigation was in progress, and as a result their thickness changed gradually. The thinnest cells had to be reassembled before each run because of the high viscosity of the compounds studied. Their thickness therefore varied somewhat from run to run. Some difficulty was experienced in avoiding air bubbles when the cells were filled. A few of the compounds, which are solid at room temperature, were melted and filled into a preheated cell which was kept a few degrees above the melting point while the spectrum was recorded.

To improve the accuracy, the runs with the thick and the intermediate cells were made on the same record; the lapse of time between the two runs was only the few seconds required to

Table I. 1-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.97	668	Weak
14.33	697.8	Very strong
13.87	721.1	Very strong
13.42	745.2	Very strong
11.90	840.3	Weak
11.05	905.7	Medium
10.35	965.9	Weak
10.22	978.7	Very weak
9.95	1005	Very weak
9.698	1031.1	Medium
9.47	1060	Very weak
9.31	1074	Medium
8.98	1134	Weak
8.646	1156.6	Weak
8.479	1179.4	Weak
8.30	1205	Weak
8.00	1250	Very weak
7.64	1309	Medium
7.39	1353	Strong
7.25	1379	Very strong
6.857	1458.4	Very strong
6.808	1468.9	Very strong
6.680	1497.0	Very strong
6.52	1534	Weak
6.29	1590	Very weak
6.22	1608	Medium
6.04	1660	Very weak
5.734	1744	Very weak
5.549	1802	Weak
5.350	1869	Weak
5.144	1944	Weak
4.916	2034	Very weak
4.59	2180	Very weak
4.29	2331	Very weak
3.75	2670	Weak
3.42	2922	Very strong
3.32	3012	Weak
2.98	3360	Very weak
2.91	3440	Very weak
2.78	3600	Very weak
2.70	3700	Very weak
2.58	3880	Very weak
2.41	4150	Weak
2.40	4170	Weak
2.37	4230	Weak
2.21	4520	Very weak
1.80	5580	Very weak
1.77	5660	Very weak

Table II. 2-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.29	700	Very strong
13.88	720.5	Very strong
13.14	761	Very strong
11.92	831.6	Weak
11.19	893.7	Weak
11.04	905.5	Medium
10.38	963.2	Weak
10.01	998.7	Weak
9.84	1016	Medium
9.71	1029.9	Medium
9.31	1074	Medium
9.19	1088.5	Medium
9.02	1109	Very weak
8.86	1129	Very weak
8.641	1157.3	Weak
8.454	1182.9	Weak
8.02	1249	Very weak
7.64	1309	Medium
7.53	1328	Weak
7.38	1355	Strong
7.25	1380	Very strong
6.859	1457.9	Very strong
6.814	1467.6	Very strong
6.685	1495.9	Very strong
6.50	1538	Weak
6.229	1605	Medium
6.00	1667	Very weak
5.740	1742	Very weak
5.551	1801	Weak
5.349	1870	Weak
5.315	1881	Very weak
5.149	2921	Weak
4.93	2028	Very weak
4.59	2180	Very weak
4.28	2336	Very weak
3.74	2674	Weak
3.50	2860	Very strong
3.42	2921	Very strong
3.31	3021	Weak
2.73	3660	Very weak
2.64	3790	Very weak
2.43	4120	Weak
2.40	4170	Weak
2.37	4230	Weak
2.32	4310	Weak
2.17	4610	Very weak
1.78	5610	Very weak
1.75	5710	Very weak

Table III. 3-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.93	670	Medium
14.29	699.8	Very strong
13.87	721.1	Very strong
13.20	757.6	Very strong
11.92	838.9	Weak
11.14	897.7	Medium
10.38	962.9	Weak
10.22	978.5	Very weak
9.98	1002.4	Very weak
9.71	1029.9	Medium
9.37	1067	Medium
9.17	1091	Weak
9.03	1107	Very weak
8.88	1126	Very weak
8.82	1134	Very weak
8.654	1155.6	Weak
8.467	1181.1	Weak
7.66	1305	Medium
7.27	1376	Very strong
6.857	1458.4	Very strong
6.824	1464.4	Very strong
6.692	1494.3	Very strong
6.50	1540	Weak
6.231	1605	Medium
5.99	1669	Very weak
5.74	1741	Very weak
5.559	1799	Weak
5.340	1873	Weak
5.149	1942	Weak
4.92	2033	Very weak
4.27	2340	Very weak
3.75	2667	Weak
3.65	2740	Very weak
3.42	2921	Very strong
3.32	3010	Weak
2.75	3640	Very weak
2.45	4080	Weak
2.41	4150	Weak
2.37	4220	Weak
2.33	4300	Weak
2.18	4590	Very weak
1.79	5600	Very weak
1.74	5740	Very weak

Table IV. 4-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.93	670	Medium
14.30	699.3	Very strong
13.86	721.5	Very strong
13.70	730	Strong
13.16	760.2	Very strong
11.91	839.6	Weak
11.23	890.5	Weak
11.02	970.4	Medium
10.38	962.9	Weak
10.21	979.4	Weak
9.96	1004	Very weak
9.704	1030.5	Medium
9.36	1068	Medium
9.01	1110	Weak
8.652	1155.8	Weak
8.467	1181.1	Weak
8.20	1220	Weak
8.00	1250	Very weak
7.64	1308	Medium
7.26	1378	Very strong
6.849	1460	Very strong
6.819	1467	Very strong
6.684	1496.1	Very strong
6.49	1540	Weak
6.30	1587	Very weak
6.224	1607	Medium
5.99	1669	Very weak
5.88	1701	Very weak
5.734	1744	Very weak
5.554	1801	Weak
5.350	1869	Weak
5.144	1944	Weak
4.92	2033	Very weak
4.58	2183	Very weak
4.42	2260	Very weak
4.27	2340	Very weak
3.73	2680	Weak
3.64	2750	Weak
3.41	2932	Very strong
3.32	3010	Weak
2.75	3640	Very weak
2.60	3850	Very weak
2.45	4080	Weak
2.41	4150	Weak
2.37	4220	Weak
2.33	4290	Weak
1.78	5610	Very weak
1.75	5720	Very weak

Table V. 5-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.91	670.7	Weak
14.30	698.3	Very strong
13.84	722.6	Very strong
13.19	758.4	Very strong
11.91	839.6	Weak
11.22	892.2	Weak
11.06	904.6	Medium
10.66	938.0	Weak
10.40	961.5	Weak
10.22	978.5	Weak
9.96	1004	Very weak
9.696	1031.4	Medium
9.34	1070.9	Medium
8.99	1112.8	Weak
8.647	1156.5	Weak
8.460	1182.0	Weak
8.02	1247.	Very weak
7.64	1309	Medium
7.23	1383	Very strong
6.855	1458.8	Very strong
6.811	1468.2	Very strong
6.680	1497.0	Very strong
6.51	1536	Weak
6.30	1587	Very weak
6.227	1610	Medium
5.99	1669	Very weak
5.740	1742	Very weak
5.567	1796	Weak
5.355	1867	Weak
5.155	1940	Weak
4.925	2030	Very weak
4.58	2180	Very weak
4.44	2250	Very weak
4.29	2330	Very weak
3.73	2678	Weak
3.65	2740	Weak
3.41	2933	Very strong
2.74	3650	Very weak
2.60	3850	Very weak
2.44	4100	Weak
2.37	4220	Weak
2.35	4260	Weak
2.32	4310	Weak
2.15	4650	Very weak
1.82	5490	Very weak
1.77	5640	Very weak
1.74	7540	Very weak

Table VI. 7-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.28	700.3	Very strong
13.84	722.5	Very strong
13.15	760.5	Very strong
11.90	840.3	Weak
11.23	890.5	Weak
11.05	905.0	Medium
10.39	962.2	Weak
10.22	978.4	Weak
10.04	996	Very weak
9.95	1005	Very weak
9.710	1030	Medium
9.357	1071	Medium
8.943	1118	Weak
8.82	1134	Very weak
8.653	1155.7	Weak
8.464	1181.5	Weak
8.00	1250	Weak
7.66	1305	Medium
7.52	1330	Weak
7.39	1353	Strong
7.26	1377	Very strong
6.816	1467.1	Very strong
6.692	1494.3	Very strong
6.49	1540	Weak
6.30	1587	Very weak
6.229	1605	Medium
6.01	1664	Very weak
5.89	1698	Very weak
5.731	1745	Very weak
5.552	1801	Weak
5.345	1871	Weak
5.149	1942	Weak
4.91	2036	Very weak
4.62	2165	Very weak
4.57	2188	Very weak
4.43	2260	Very weak
4.28	2340	Very weak
3.80	2630	Very weak
3.72	2688	Weak
3.64	2747	Weak
3.49	2866	Very strong
3.41	2933	Very strong
3.32	3012	Medium
2.92	3420	Weak
2.73	3660	Very weak
2.57	3890	Very weak
2.43	4120	Weak
2.35	4260	Weak
2.33	4290	Weak
2.30	4350	Very weak
2.15	4650	Very weak
1.75	5710	Very weak
1.73	5780	Very weak

Table VII. 9-Phenyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
14.27	701	Very strong
13.86	721.1	Very strong
13.14	761	Very strong
11.90	840.3	Weak
11.23	890.4	Weak
11.05	904.8	Medium
10.38	962.9	Weak
10.21	979.0	Weak
10.07	993	Weak
9.94	1006	Very weak
9.705	1030.4	Medium
9.33	1072.2	Medium
8.93	1120.5	Weak
8.644	1156.9	Weak
8.458	1182.3	Weak
8.00	1250	Very weak
7.66	1305	Medium
7.52	1330	Weak
7.258	1377.8	Very strong
6.849	1460.1	Very strong
6.816	1467	Very strong
6.684	1496	Very strong
6.50	1538	Very weak
6.30	1587	Very weak
6.225	1606	Very strong
6.01	1664	Very weak
5.734	1744	Very weak
5.555	1800	Weak
5.355	1867	Weak
5.155	1940	Weak
4.92	2033	Very weak
4.57	2190	Very weak
4.44	2250	Very weak
4.29	2330	Very weak
3.73	2678	Weak
3.64	2747	Very weak
3.51	2849	Very strong
3.42	2921	Very strong
2.71	3690	Very weak
2.58	3880	Very weak
2.44	4100	Weak
2.38	4200	Weak
2.35	4260	Weak
2.30	4350	Weak
2.14	4670	Very weak
1.77	5660	Very weak
1.74	5740	Very weak

bring the instrument back to the beginning of each wave-length interval over which a given slit width was used. This ensured similar temperature and sensitivity, as well as identical slit width, for the two absorption curves.

The spectrometer was calibrated by means of known wave lengths of absorption lines of ammonia and carbon dioxide. In each record correction was made for slight shifts caused by temperature variation. Correction for stray radiation was made with the aid of an average curve constructed from measurements on a large number of hydrocarbons. During the latter part of this work the correction for stray radiation amounted to 1.0% of the deflection, I_0 , obtained with no absorbing material in front of the slit, at 10 μ , 2.0% at 13 μ , 5% at 14 μ , and 20% at 15 μ . The per cent transmittance was determined and plotted against wave length in the usual manner.

RESULTS

Per cent transmittance curves for 1-, 2-, 3-, 4-, 5-, 7-, and 9-phenyleicosane, covering the region from 2 to 15 μ , are shown, on a uniform wave-length scale, in Figures 1 to 7. In the lower right-hand corner of each figure are given the thicknesses of the cells used as well as the approximate temperature of the liquid. The per cent transmittance curves for the corresponding cyclohexyleicosanes are given in Figures 8 to 14. In the first columns of Tables I to XIV are listed the wave-lengths of the absorption maxima (or "shoulders") as measured on the spectrometer records. In the second column of each table are given the corresponding wave numbers. The third column gives a rough estimate of the intensity of each absorption maximum made in the following manner:

An absorption maximum is designated as very weak if the per cent transmittance obtained with the 0.06-mm. cell lies between

100 and 80; weak if the per cent transmittance lies between 80 and 60, medium if the transmittance lies between 60 and 40%, strong if the transmittance lies between 40 and 20%, and very strong if the transmittance observed with the 0.06-mm. cell is less than 20%. Shoulders on the sides of stronger absorption maxima have usually been given an intensity rating corresponding to 20 units less than the observed per cent transmittance.

The inaccuracy in the wave-length measurements varies from about $\pm 0.005 \mu$ at 14 μ to $\pm 0.03 \mu$ at 3 μ . It will, of course, de-

Table VIII. 1-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.870	721.0	Strong
13.09	763.9	Weak
12.20	819.7	Very weak
11.853	843.7	Medium
11.55	865.8	Very weak
11.250	888.9	Medium
10.95	913.2	Very weak
10.80	925.9	Very weak
10.41	960.6	Weak
9.682	1032.8	Very weak
9.269	1078.9	Weak
8.88	1126	Very weak
8.73	1145	Very weak
8.53	1172	Very weak
8.40	1190	Very weak
7.907	1264.7	Medium
7.66	1305	Medium
7.38	1355	Medium
7.24	1381	Medium
6.899	1449.5	Very strong
6.821	1466.1	Very strong
6.65	1504	Weak
4.905	2039	Very weak
4.581	2183	Very weak
4.474	2235	Very weak
3.746	2670	Medium
3.63	2750	Medium
3.476	2877	Very strong
3.405	2937	Very strong
2.94	3400	Weak
2.33	4290	Weak
2.30	4350	Weak

Table IX. 2-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.864	721.3	Very strong
11.96	835.8	Weak
11.72	854.1	Weak
11.23	890.6	Strong
10.95	913.2	Very weak
10.79	926.8	Very weak
10.61	942.9	Very weak
10.41	961	Weak
10.01	990	Weak
9.712	1029.7	Weak
9.39	1065	Very weak
9.31	1074.5	Weak
9.22	1085	Very weak
8.89	1125	Very weak
8.647	1156.5	Weak
8.42	1188.4	Weak
8.065	1239.9	Very weak
7.911	1264.1	Medium
7.66	1305	Medium
7.24	1381	Very strong
6.889	1451.6	Very strong
6.849	1460.1	Very strong
6.815	1467.8	Very strong
4.92	2035	Very weak
4.57	2190	Very weak
4.49	2230	Very weak
3.96	2530	Very weak
3.84	2600	Very weak
3.75	2667	Medium
3.48	2872	Very strong
3.40	2945	Very strong
2.92	3420	Weak
2.73	3660	Very weak
2.67	3750	Very weak
2.52	3970	Very weak
2.38	4200	Weak
2.35	4250	Weak
2.30	4350	Weak
1.79	5590	Very weak
1.75	5710	Very weak
1.72	5810	Very weak

Table XI. 4-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.872	720.8	Very strong
13.57	737	Weak
12.92	774	Weak
12.48	801	Very weak
11.96	836.1	Very weak
11.80	847.5	Weak
11.21	892.1	Medium
10.28	973	Very weak
10.19	981	Weak
9.69	1031.7	Weak
9.62	1040	Very weak
9.48	1055	Very weak
9.30	1075.7	Weak
9.18	1089	Very weak
9.894	1124.4	Weak
8.679	1152.2	Weak
8.46	1182	Weak
8.26	1211	Very weak
8.08	1237.8	Weak
7.905	1265.0	Medium
7.66	1305	Medium
7.37	1357	Weak
7.26	1377	Very strong
7.07	1414	Weak
6.889	1451.6	Very strong
6.857	1458.4	Very strong
6.816	1467.1	Very strong
6.05	1653	Very weak
4.89	2040	Very weak
4.56	2190	Very weak
4.46	2240	Very weak
4.13	2420	Very weak
3.84	2600	Very weak
3.75	2667	Medium
3.64	2750	Weak
3.50	2860	Very strong
3.42	2931	Very strong
2.94	3400	Weak
2.69	3720	Very weak
2.65	3770	Very weak
2.52	3970	Very weak
2.35	4260	Weak
2.32	4310	Weak
2.28	4380	Weak
1.79	5590	Very weak
1.75	5710	Very weak
1.72	5820	Very weak

Table X. 3-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.852	721.9	Strong
13.22	756.4	Weak
12.531	789.0	Weak
11.84	844.6	Weak
11.78	848.9	Weak
11.218	891.4	Medium
10.90	917.4	Very weak
10.46	956.0	Weak
9.710	1029.9	Weak
9.57	1045	Weak
9.38	1066	Weak
9.245	1081.7	Weak
8.882	1125.9	Weak
8.72	1147	Very weak
8.653	1155.7	Weak
8.400	1190.5	Weak
7.895	1266.6	Medium
7.64	1309	Medium
7.38	1355	Medium
7.23	1383	Strong
6.883	1452.9	Very strong
6.813	1467.8	Very strong
4.91	2040	Very weak
4.57	2190	Very weak
4.47	2240	Very weak
3.734	2678	Medium
3.63	2750	Weak
3.494	2862	Very strong
3.420	2924	Very strong
2.59	4180	Weak
2.33	4290	Weak
2.30	4350	Weak

Table XII. 5-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.85	722.0	Strong
13.08	764.5	Weak
11.848	844.0	Weak
11.602	861.9	Very weak
11.222	891.1	Medium
10.98	910.7	Weak
10.309	970.7	Weak
9.69	1032.0	Weak
9.53	1049	Weak
9.42	1062	Weak
9.23	1083	Weak
8.876	1126.6	Weak
8.672	1153.1	Weak
8.06	1241	Weak
7.902	1265.5	Medium
7.65	1307	Medium
7.43	1346	Medium
7.24	1381	Strong
6.87	1456	Very strong
6.813	1467.8	Very strong
4.92	2030	Very weak
4.58	2180	Very weak
4.47	2240	Very weak
3.83	2610	Weak
3.47	2880	Very strong
3.420	2924	Very strong
3.74	2670	Medium
2.95	3390	Weak
2.37	4220	Weak
2.34	4270	Weak
2.30	4350	Weak

Table XIII. 7-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.844	722.3	Strong
12.728	785.7	Weak
11.86	843.2	Weak
11.218	891.4	Medium
10.06	994.0	Weak
9.688	1032.2	Weak
9.28	1078	Weak
9.03	1107	Weak
8.882	1125.9	Weak
8.692	1150.5	Weak
8.04	1244	Weak
7.895	1266.6	Medium
7.66	1305	Medium
7.38	1355	Medium
7.25	1379	Strong
6.88	1453	Very strong
6.813	1467.8	Very strong
4.92	2030	Very weak
4.26	2350	Very weak
4.13	2420	Very weak
3.83	2610	Weak
3.734	2678	Medium
3.494	2862	Very strong
3.420	2924	Very strong
2.92	3420	Weak
2.61	3830	Very weak
2.37	4220	Weak
2.33	4290	Weak
2.29	4370	Weak

Table XIV. 9-Cyclohexyleicosane (Liquid)

Wave Length, Microns	Wave No., Cm. ⁻¹	Intensity
13.844	722.3	Strong
11.855	843.5	Weak
11.42	875.7	Weak
11.218	891.4	Medium
10.319	959.1	Weak
10.11	989.1	Very weak
9.69	1032	Weak
9.39	1065	Weak
9.29	1077	Weak
8.96	1116	Very weak
8.876	1126.6	Very weak
8.692	1150.5	Very weak
8.55	1170	Very weak
8.374	1194.2	Weak
8.24	1214	Weak
8.05*	1242	Weak
7.895	1266.6	Medium
7.65	1307	Medium
7.38	1355	Medium
7.23	1383	Strong
6.89	1451	Very strong
6.813	1467.8	Very strong
4.91	2040	Very weak
3.91	2560	Very weak
3.75	2670	Medium
3.64	2750	Weak
3.494	2862	Very strong
3.420	2924	Very strong
2.94	3400	Weak
2.37	4220	Weak
2.35	4260	Weak
2.29	4370	Weak

Table XV. Wave Lengths Characteristic of Structural Group

Phenyl, μ Intensities ^a	Cyclohexyl, μ Intensities ^a	Chain, μ Intensities ^a
14.29 vs	11.85 w	13.85 vs
13.16 vs	11.22 m	12.75 vw
11.90 w	8.88 w	11.24 m
11.05 w	8.67 w	9.70 w
10.39 w	8.40 w	9.30 m
10.22 w	7.90 m	7.65 m
9.95 vw		7.39 m
9.70 m		7.25 s
9.34 m		6.86 s
8.65 w		6.82 s
8.47 w		6.00 w
6.68 s		5.6 vw
6.50 w		4.30 vw
6.30 vw		4.91 w
6.23 m		4.58 vw
6.00 vw		4.43 vw
5.88 vvw		4.28 vw
5.73 w		3.94 vw
5.55 w		3.83 w
5.50 vw		3.74 m
5.35 w		3.49 s
5.15 w		3.42 s
5.10 vvw		2.92 w
4.28 w		2.74 vw
3.32 m		2.43 vw
2.74 vw		2.40 w
2.43 w		2.35 w
2.18 vw		2.30 w

^a vs. Very strong.
s. Strong
m. Medium.

w. Weak.
vw. Very weak.
vvw. Very very weak.

pend somewhat upon the shape of the absorption maximum and upon its proximity to other maxima.

In the region from 5 to 6 μ the phenyleicosanes have a number of rather intense bands. The cyclohexyleicosanes, on the other hand, have only weak bands in this region. Because the residual water vapor present in the spectrometer gave rise to a number of absorption lines in this region, the detection and measurement of weak bands is somewhat difficult here. The data on the weak bands of the cyclohexyleicosanes in this region are therefore less accurate than those of similar bands in other regions, and some of the weakest bands may have escaped observation.

ASSIGNMENT OF CERTAIN BANDS TO STRUCTURAL GROUPS

The spectra of the fourteen compounds were carefully compared. It was found that a number of absorption bands occur, with only minor variation in spectral position and intensity, in the spectra of all of the phenyleicosanes but not in the spectra of the cyclohexyleicosanes. These bands must be associated with molecular normal vibrations in which only atoms within the phenyl ring, or attached to it, have appreciable amplitudes. This conclusion is supported by the finding that most of these bands occur also in other alkylbenzenes, in particular in the few other phenyl derivatives of long-chain normal paraffins for which the infrared spectra have been determined. Similarly, a few bands could be ascribed to vibrations of the cyclohexyl group. Finally, a considerable number of bands were found to occur in the spectra of all the compounds studied, as well as in the spectra of normal paraffins. These bands must be associated with normal vibrations which are limited essentially to the paraffin chain.

In Table XV are listed the wave lengths and wave numbers of the bands which are characteristic of one of the structural parts of the molecules in question. Rough indications are given of their intensities.

Phenyl Vibrations

- 14.29 μ . Shifted to 14.34 μ in 1-phenyleicosane.
13.16 μ . Shifted to 13.42 μ in 1-phenyleicosane.
11.90 μ . In the spectra of methyl-, ethyl-, *n*-propyl-, *n*-butyl-, and *n*-hexylbenzene, a similar band occurs which shifts from 11.85 to 11.90 μ as the length of the alkyl chain increases.
11.05 μ . Shifted to 11.14 μ in 3-phenyleicosane.

10.39 μ . Shifted to 10.36 μ and enhanced in 1-phenyleicosane, as well as in ethyl- and *n*-butylbenzene.

9.95 μ . In 2-phenyleicosane this band is either obscured by the shoulder at 9.84 μ or shifted to 10.01 μ and intensified. In 7- and 9-phenyleicosane it appears as a very weak shoulder.

9.70 μ . A band is found at this wave length also in the cyclohexyleicosanes. However, the intensity is much higher in the phenyleicosanes. Moreover, other alkylbenzenes absorb at this wave length.

9.34 μ . A band occurs at approximately this wave length in the spectra of both groups of compounds, but is much more intense in the phenyleicosanes.

6.00 μ . That a phenylvibration, as well as one associated with the paraffin chain, occurs in this position is indicated by the fact that the absorption maximum is stronger in the phenyleicosanes than in the cyclohexyleicosanes and by the presence of a band in some of the branched alkylbenzenes.

5.88 μ . Enhanced in 4- and 7-phenyleicosane.

5.55 μ . A weak, sharp band which occurs also in methyl-, ethyl-, *n*-propyl-, and *n*-butylbenzene, 2-phenyloctane, 7-phenyltridecane, and 9-phenylheptadecane.

5.50 μ . A very weak shoulder which occurs also in the compounds just mentioned. In benzene a strong, sharp band is found at 5.51 μ .

5.10 μ . Very weak shoulder. In benzene a strong, sharp band occurs at 5.11 μ .

4.28 μ . Enhanced in the phenyleicosanes, indicating that a phenyl band is superposed upon a chain vibration. In benzene a sharp band is found at 4.30 μ .

2.74 μ . Enhanced in all but one of the phenyleicosanes, indicating the superposition of a phenyl and a chain vibration. Its absence in 1-phenyleicosane is surprising, not least because it occurs in methyl-, *n*-hexyl-, and *n*-octadecylbenzene, as well as in benzene.

2.43 μ . Enhanced in the phenyleicosanes, indicating superposition of phenyl and chain frequencies. Benzene has a strong, sharp band at 2.46 μ .

2.18 μ . The wave length decreases as the phenyl ring moves toward the middle of the *n*-eicosane chain. Thus, the band is found at 2.21 μ in 1-phenyleicosane and at 2.14 μ in 9-phenyleicosane. In 4-phenyleicosane this band is absent; in 3-phenyleicosane it appears as a faint shoulder. Benzene has a band at 2.19 μ .

Cyclohexyl Vibrations

11.85 μ . In 2-cyclohexyleicosane this band is split into two components, one at 11.72 μ and the other at 11.96 μ . No splitting occurs in 2-cyclohexyloctane. This band is found also in all other alkylcyclohexanes investigated.

11.22 μ . Long-chain *n*-paraffins also have a band at approximately this wave length. That a cyclohexyl vibration occurs here is shown by the fact that the absorption maximum is much more intense in the cyclohexyleicosanes than in the phenyl-

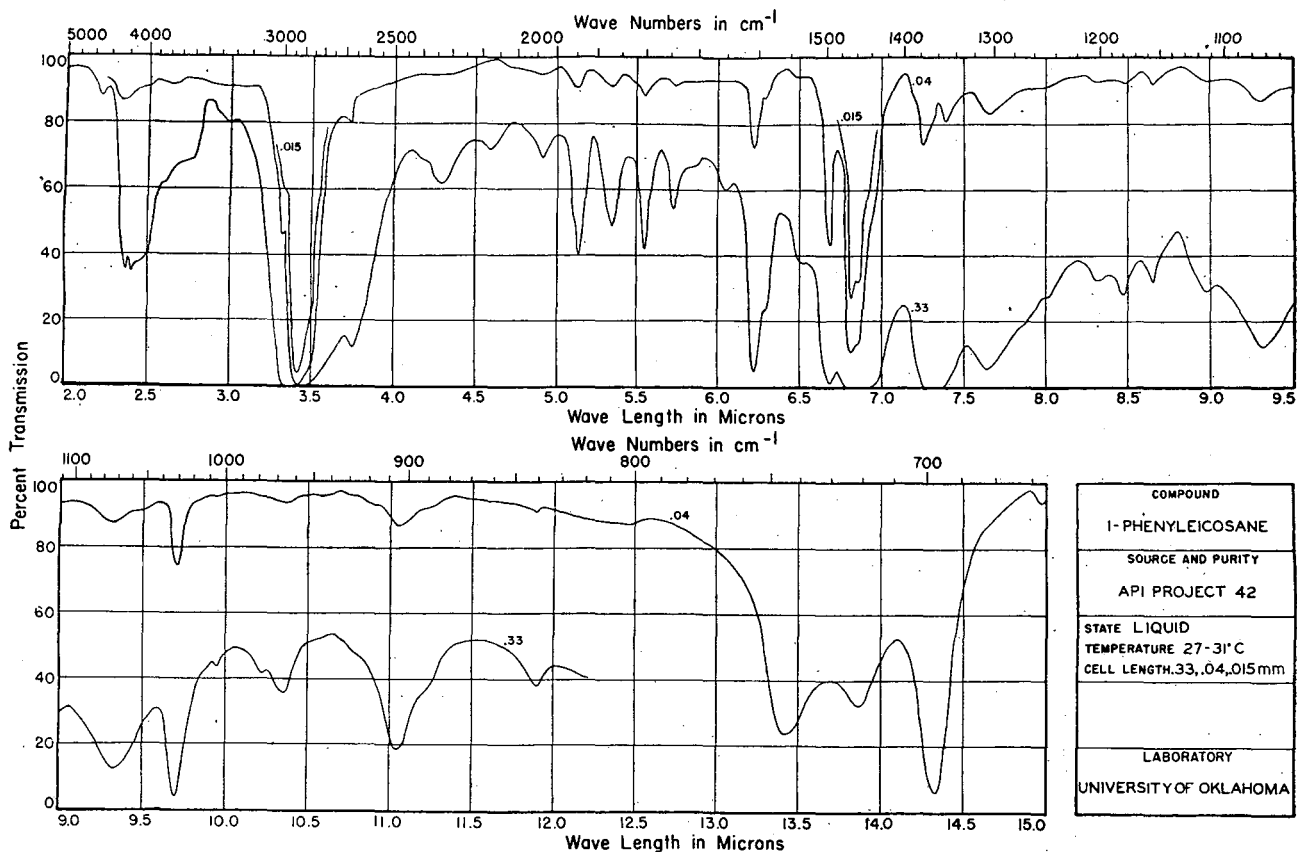


Figure 1. Infrared Absorption Spectrum of 1-Phenyleicosane

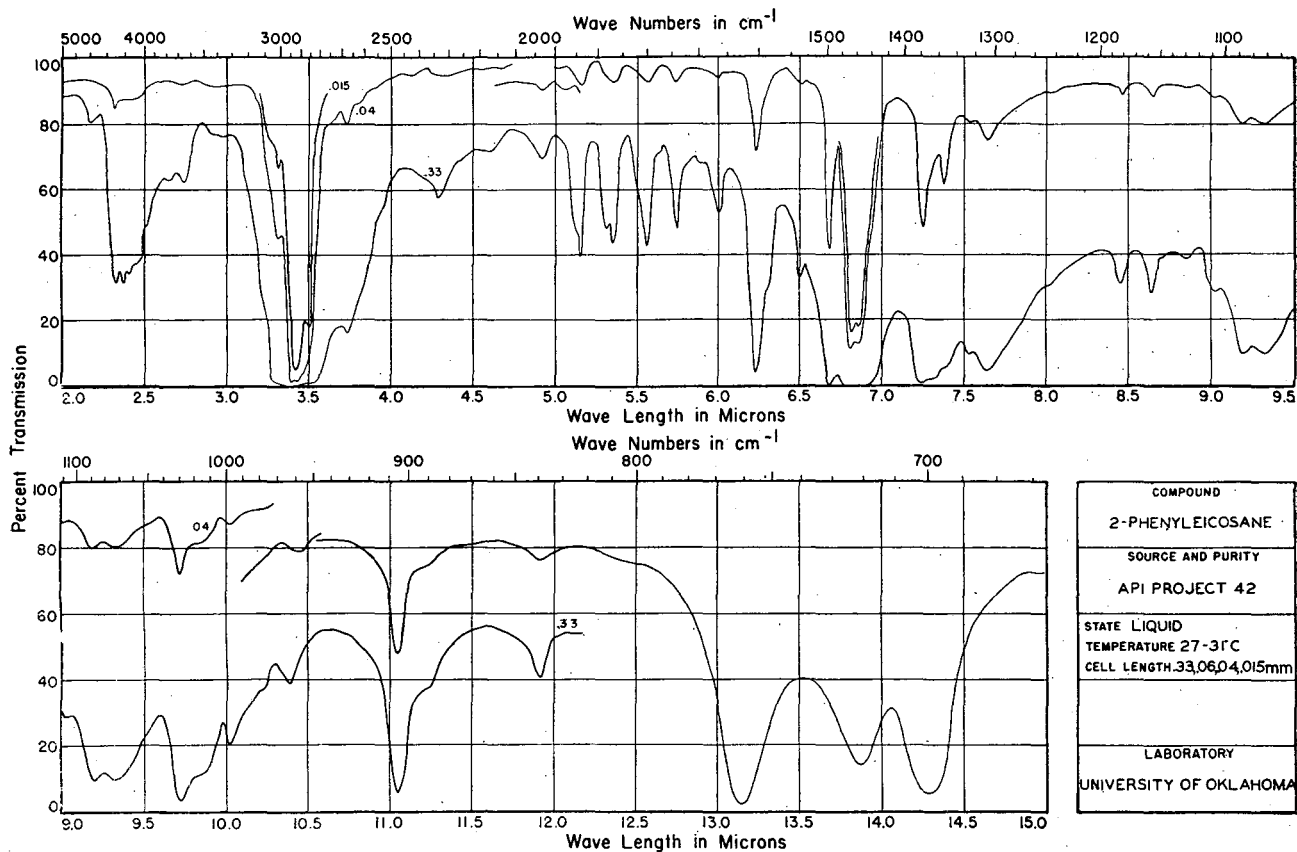


Figure 2. Infrared Absorption Spectrum of 2-Phenyleicosane

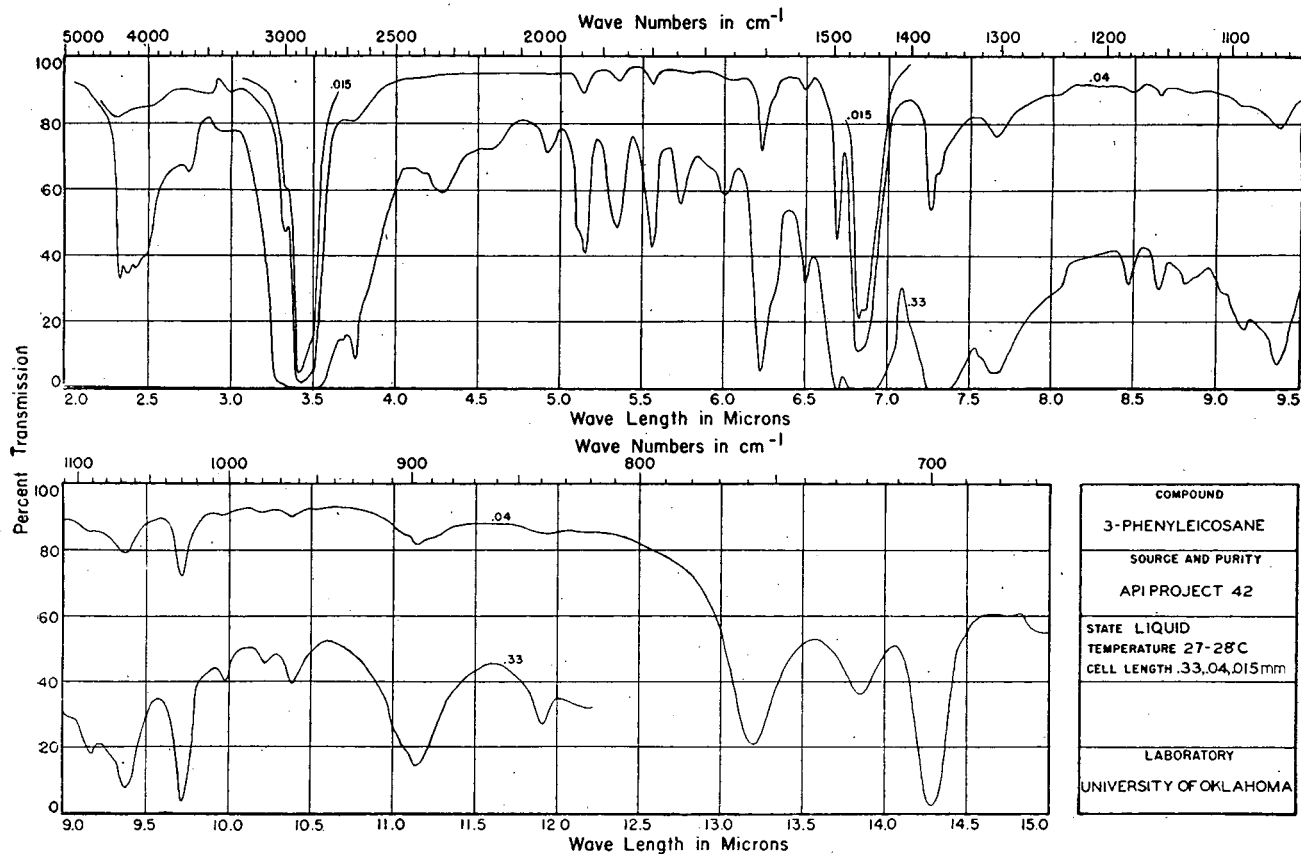


Figure 3. Infrared Absorption Spectrum of 3-Phenyleicosane

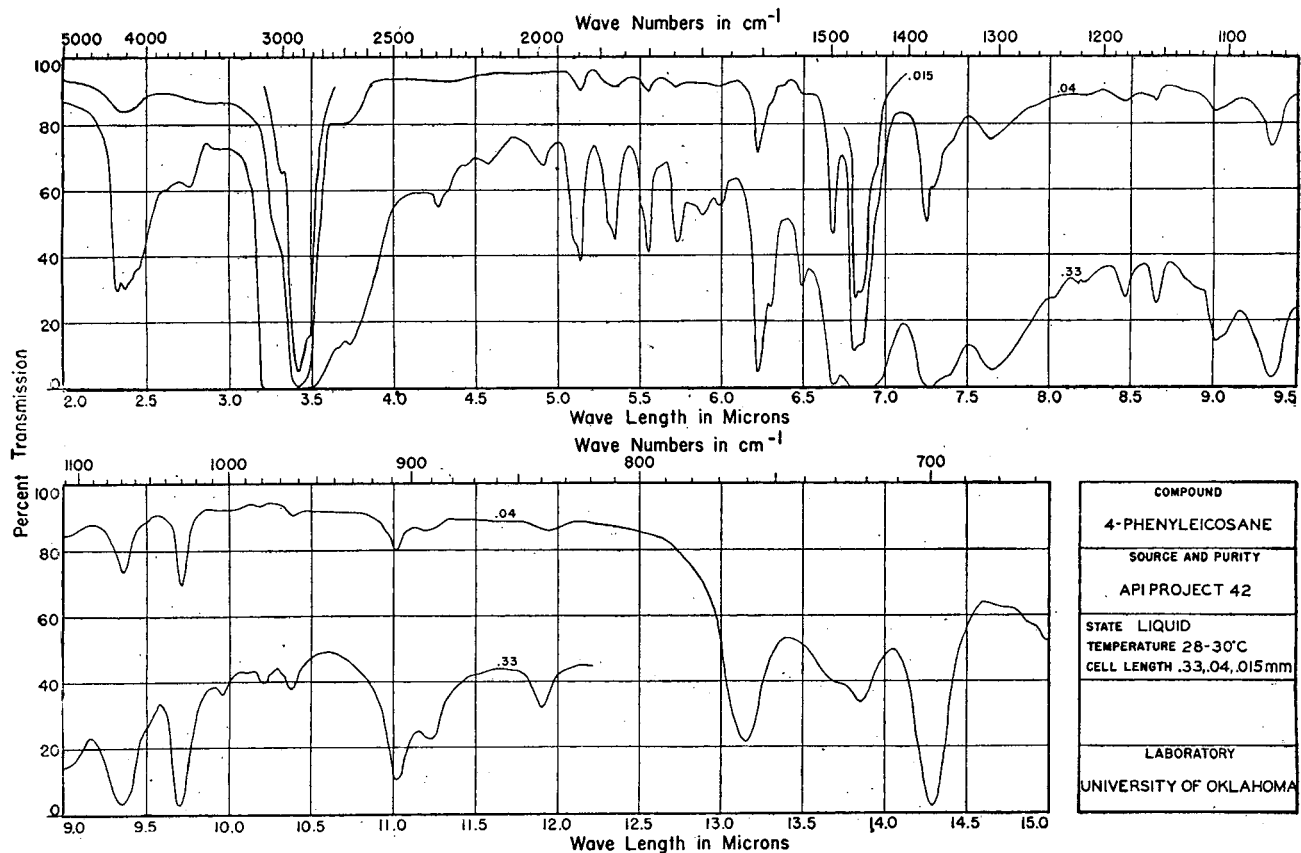


Figure 4. Infrared Absorption Spectrum of 4-Phenyleicosane

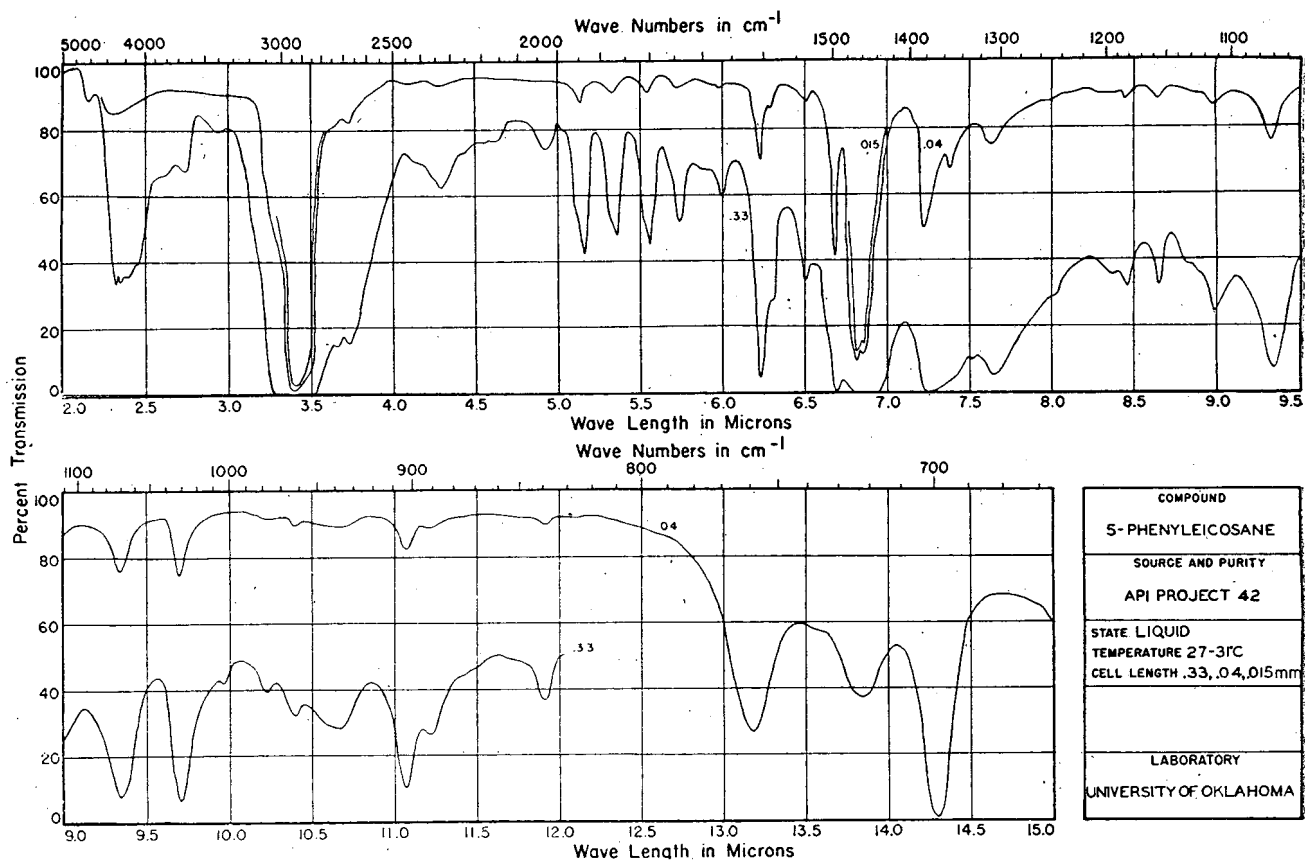


Figure 5. Infrared Absorption Spectrum of 5-Phenyleicosane

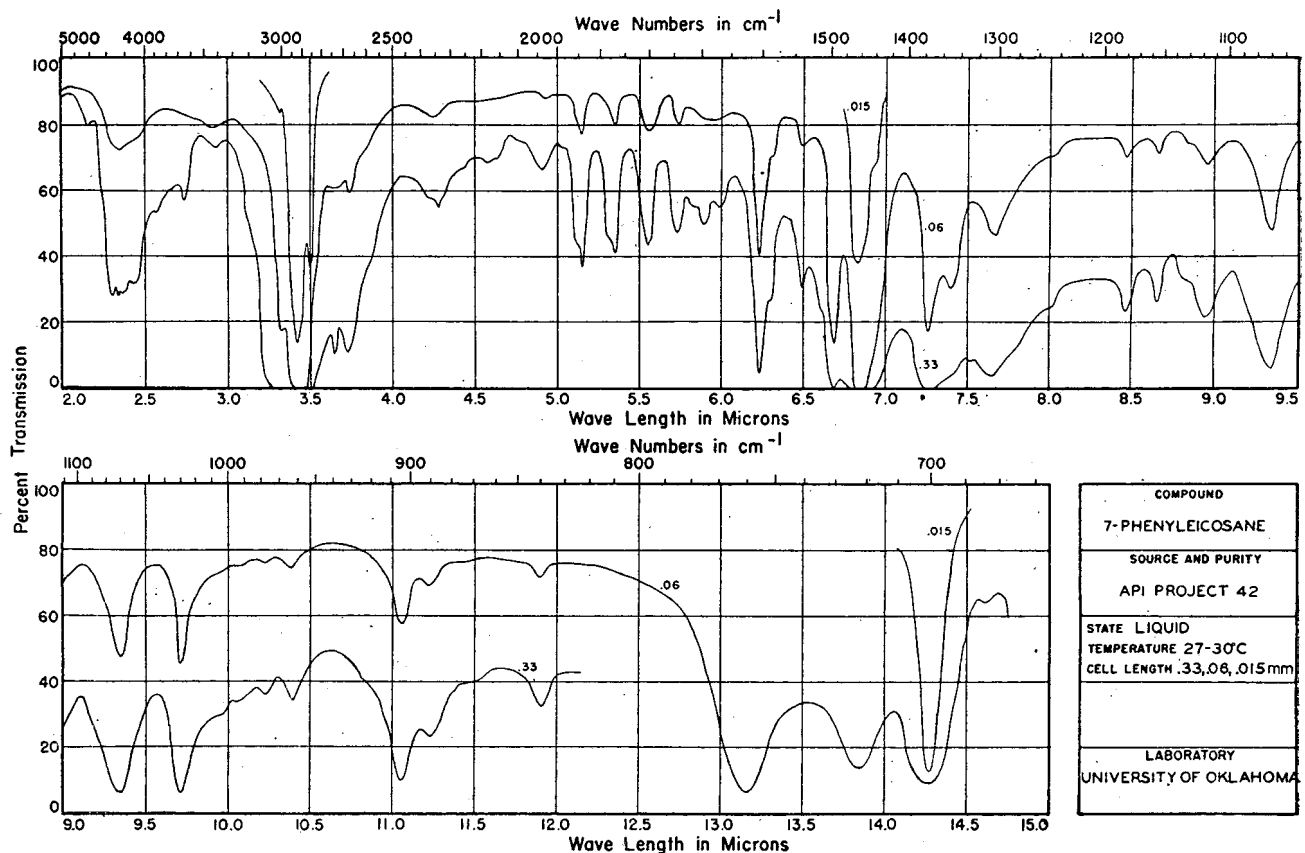


Figure 6. Infrared Absorption Spectrum of 7-Phenyleicosane

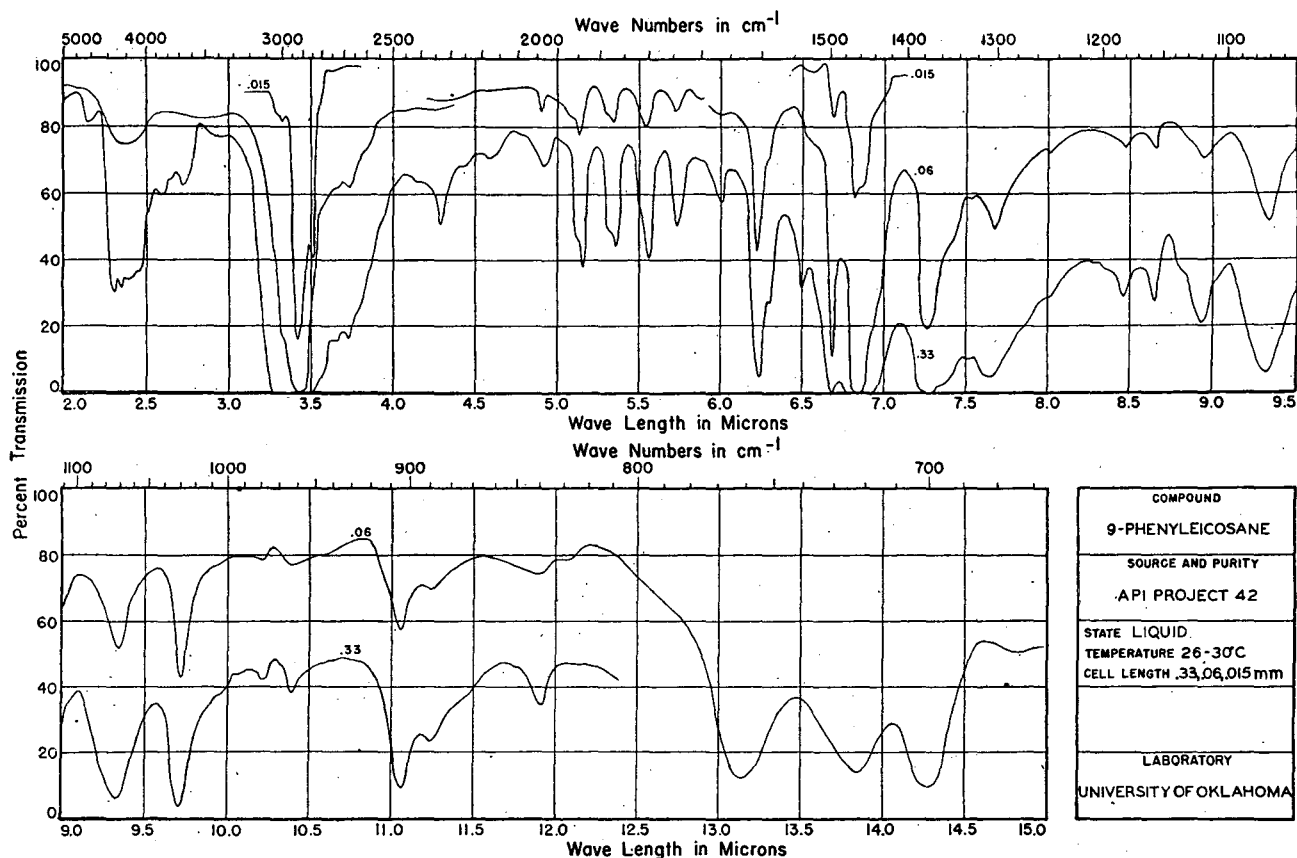


Figure 7. Infrared Absorption Spectrum of 9-Phenyleicosane

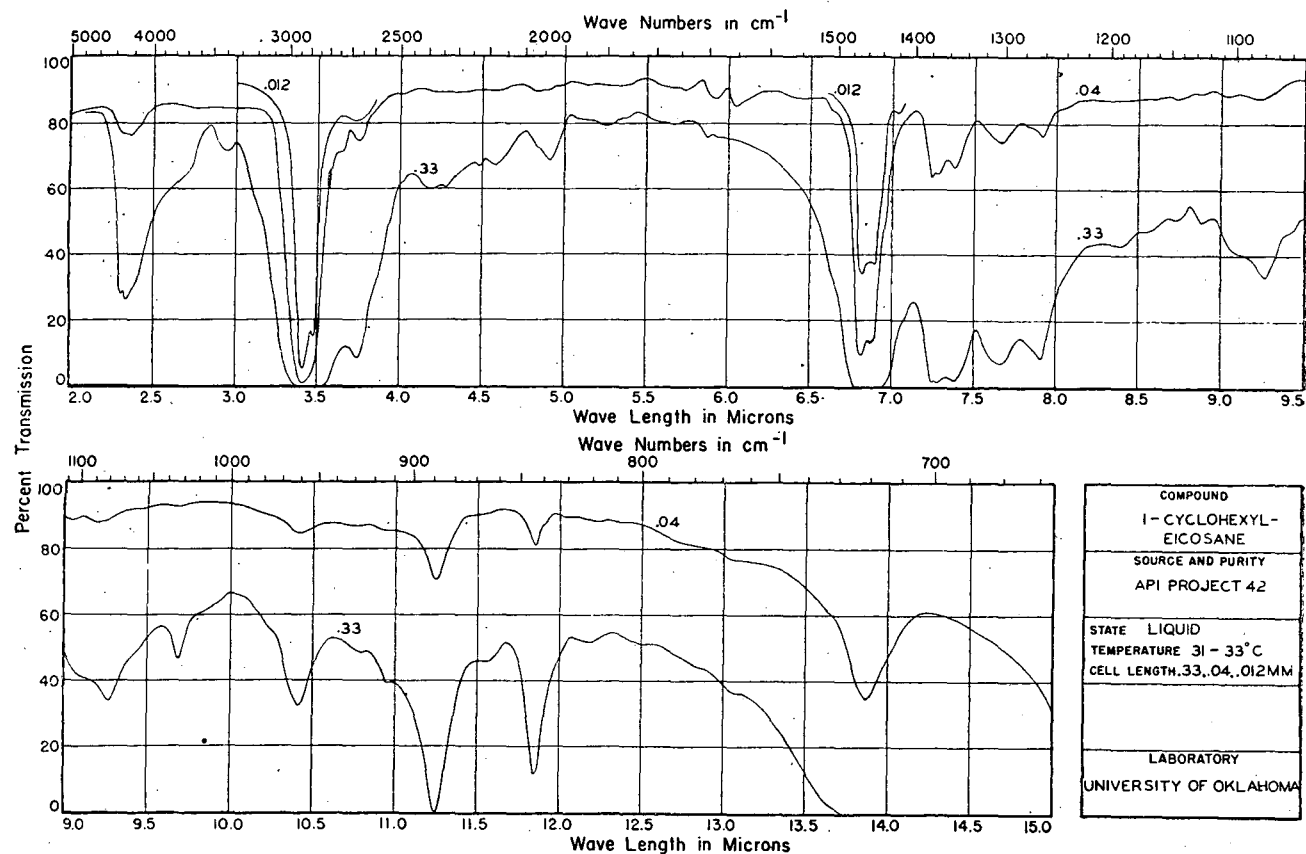


Figure 8. Infrared Absorption Spectrum of 1-Cyclohexyleicosane

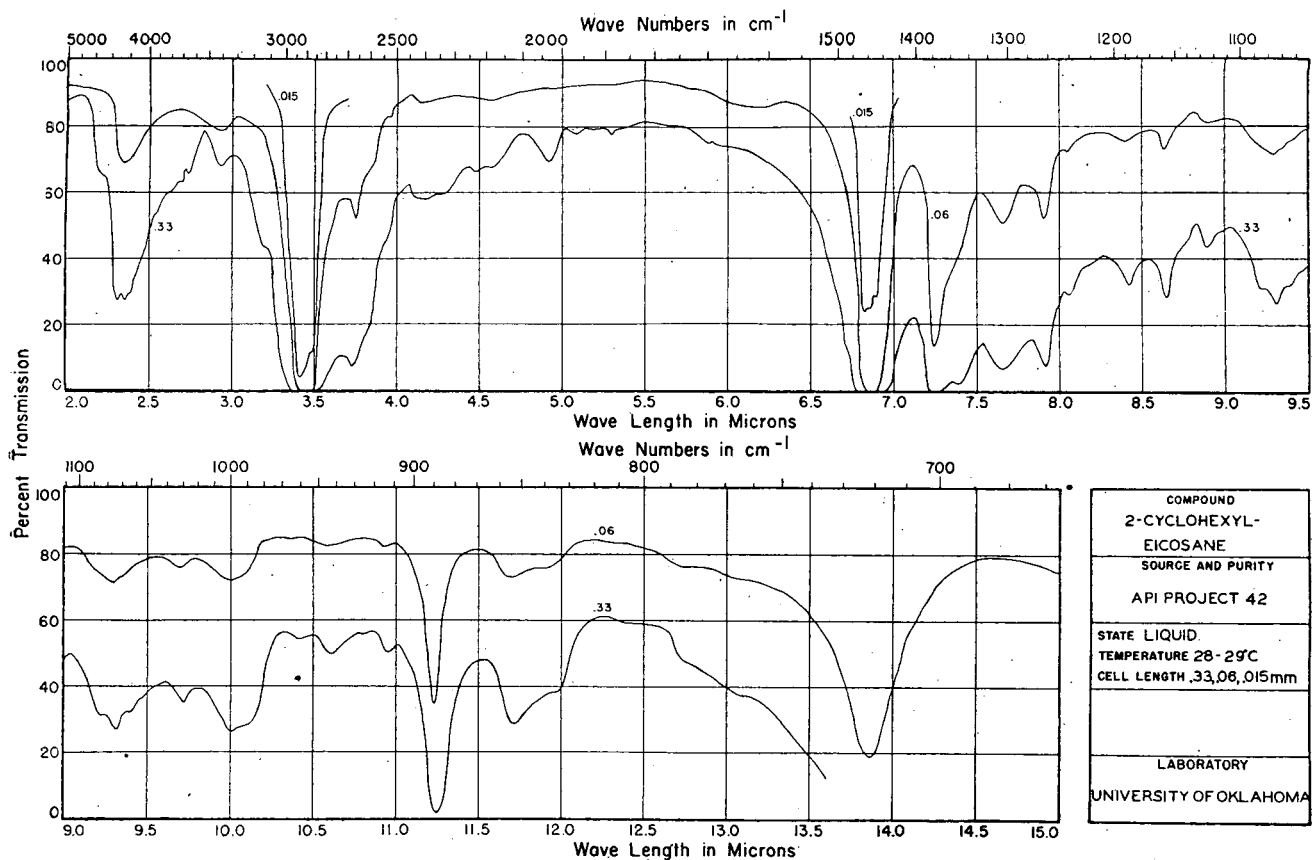


Figure 9. Infrared Absorption Spectrum of 2-Cyclohexyleicosane

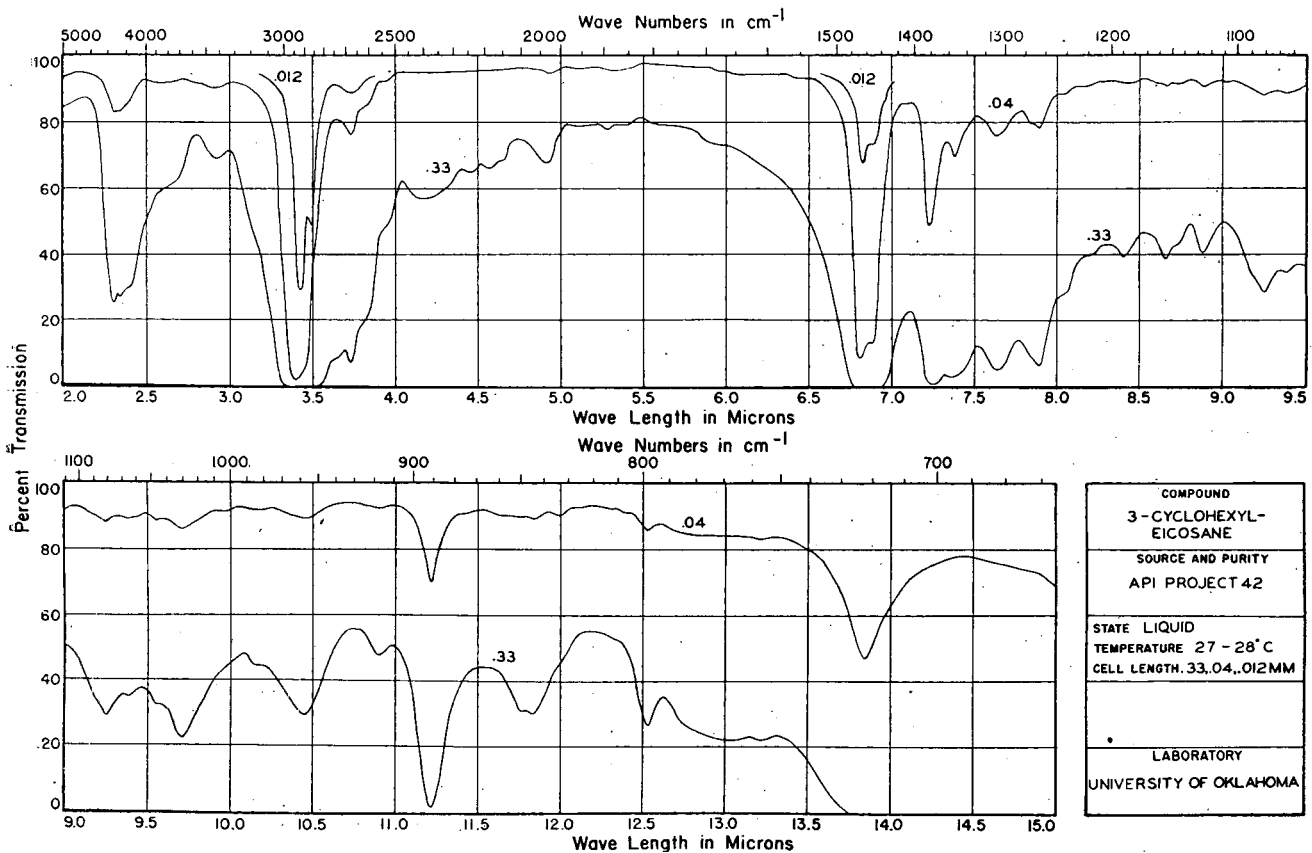


Figure 10. Infrared Absorption Spectrum of 3-Cyclohexyleicosane

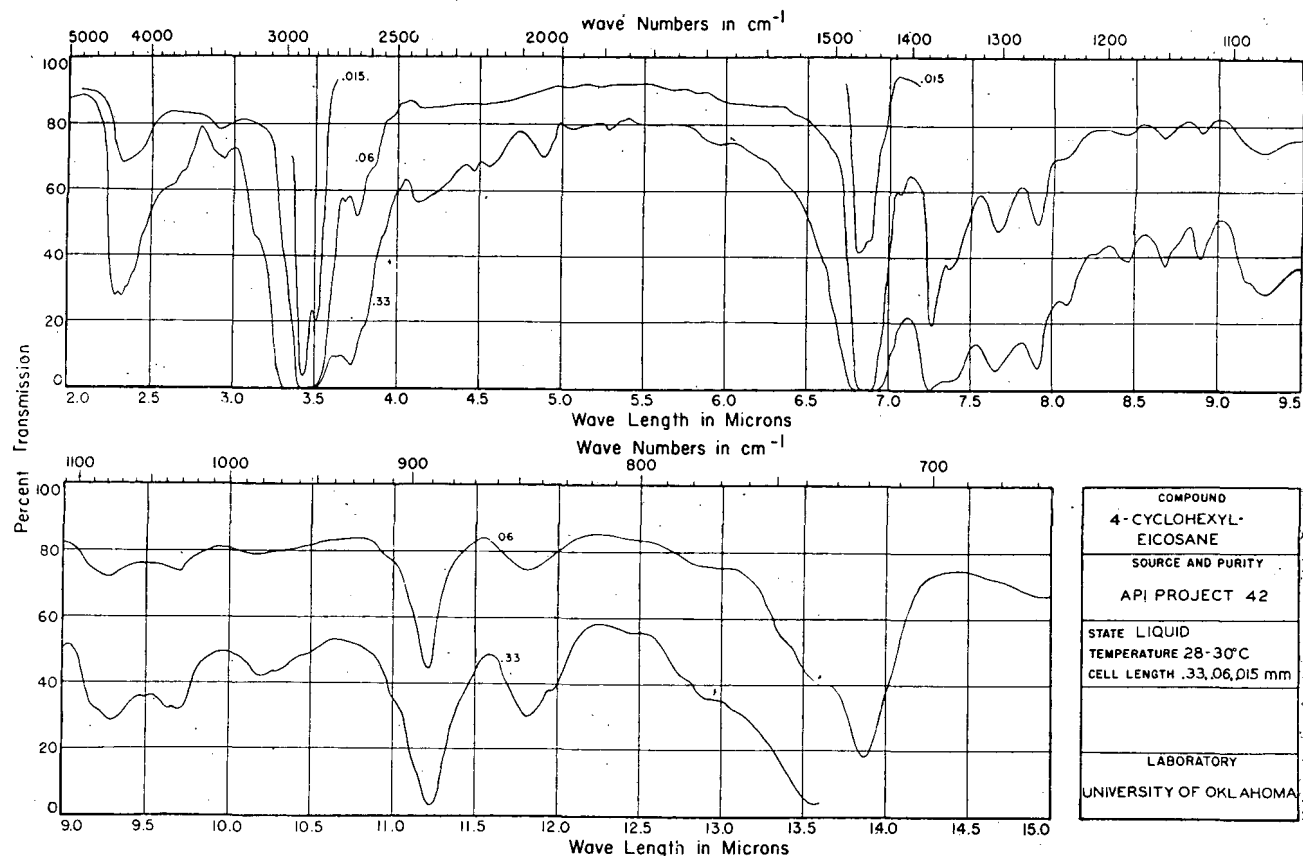


Figure 11. Infrared Absorption Spectrum of 4-Cyclohexyleicosane

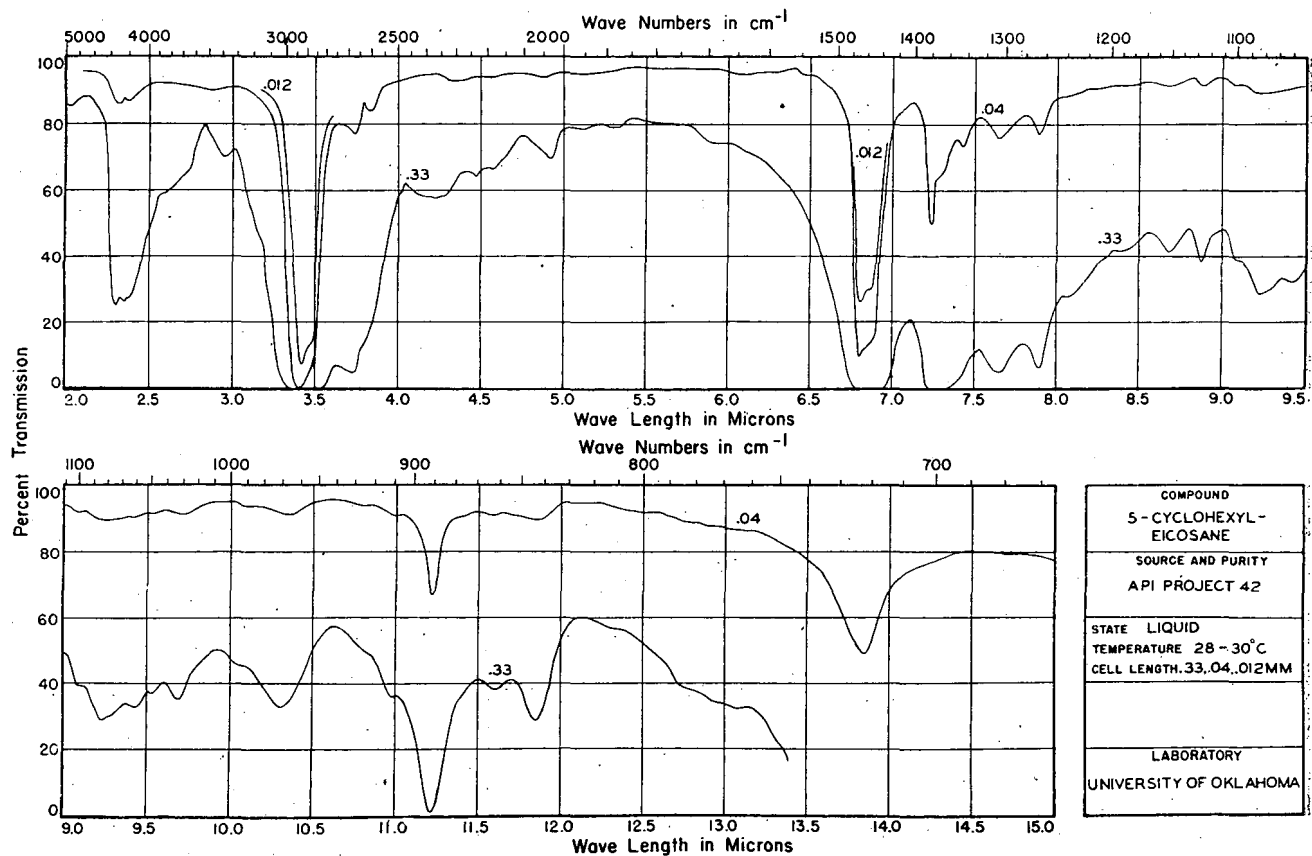


Figure 12. Infrared Absorption Spectrum of 5-Cyclohexyleicosane

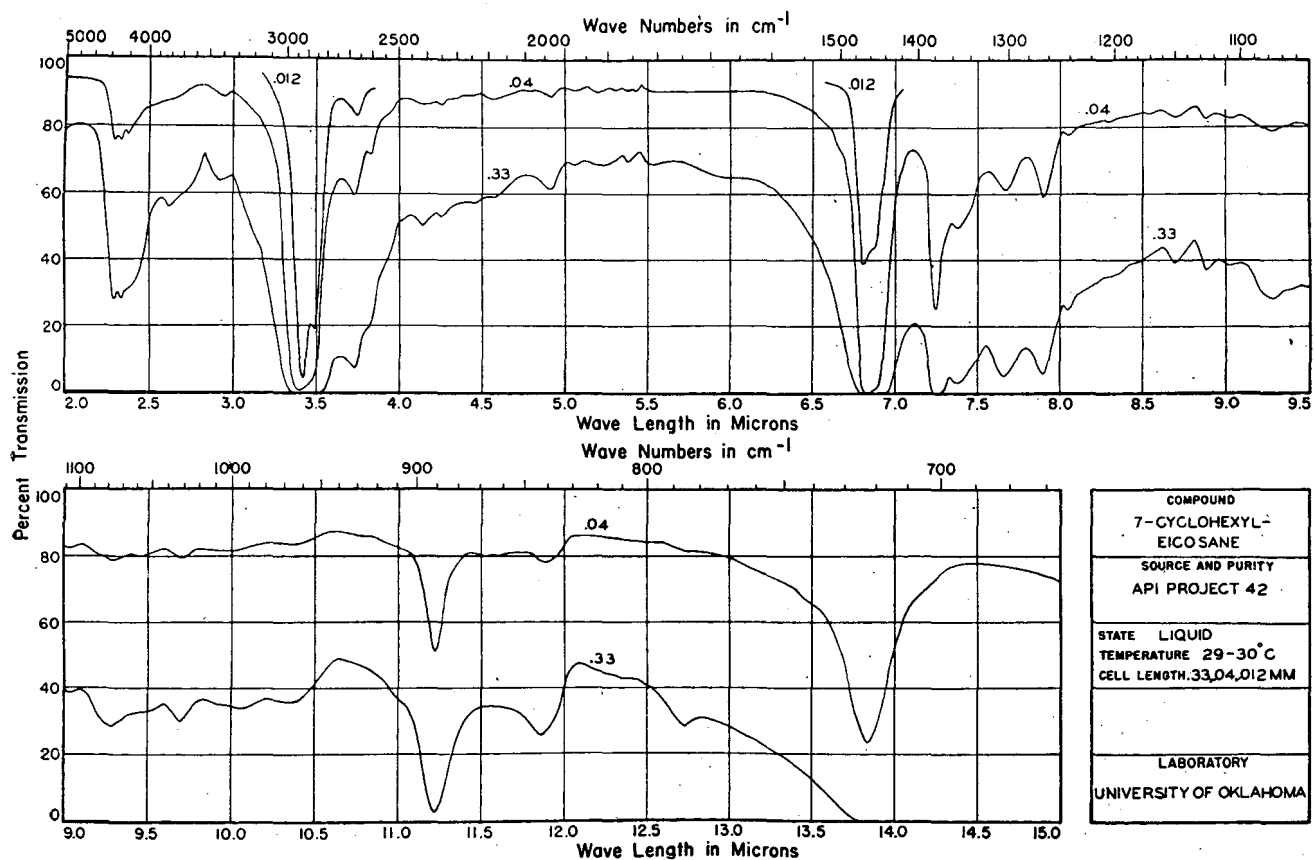


Figure 13. Infrared Absorption Spectrum of 7-Cyclohexyleicosane

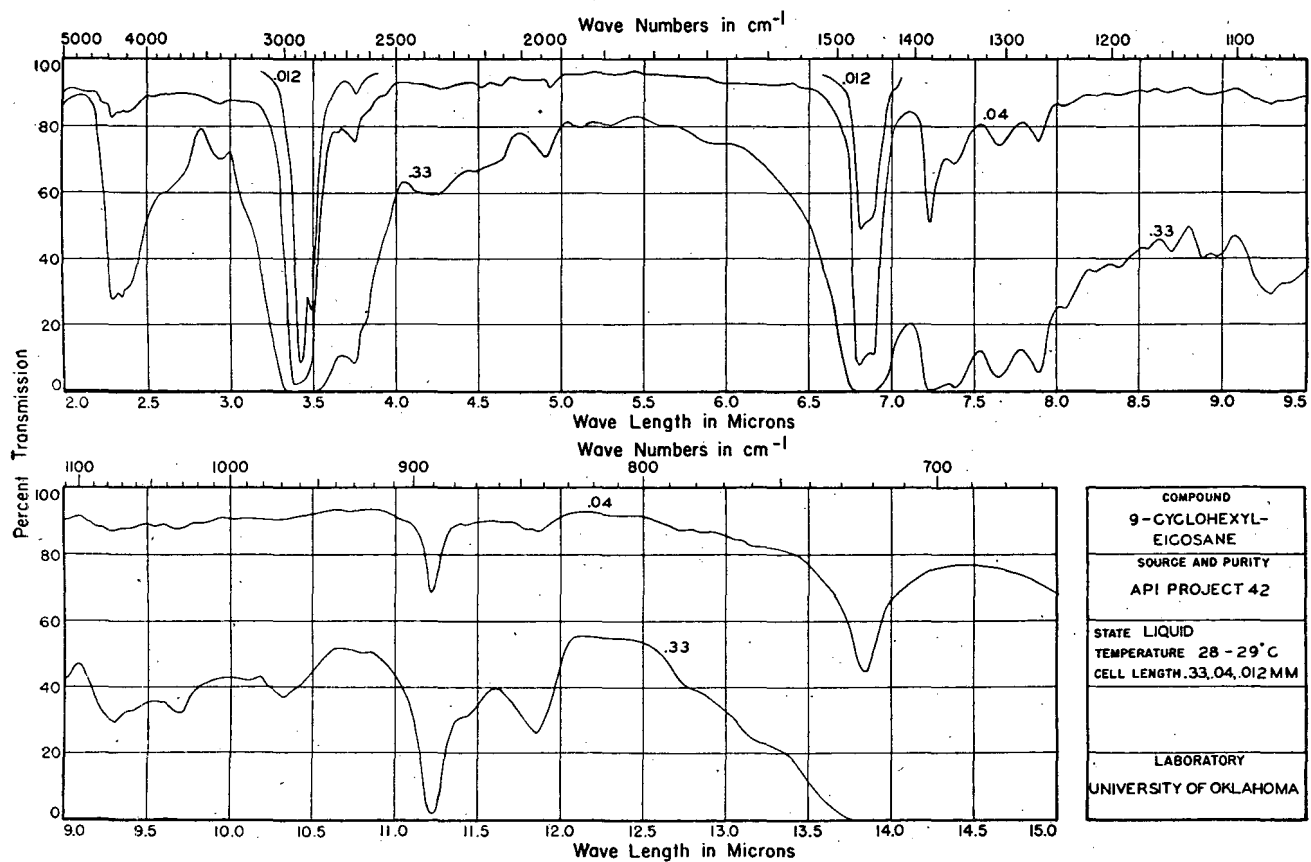


Figure 14. Infrared Absorption Spectrum of 9-Cyclohexyleicosane

eicosanes. Occurs also in all other alkylcyclohexanes investigated.

8.88 μ . That this band is associated with the cyclohexyl group is supported by the fact that bands occur at 8.87 μ in 1,2-dicyclohexylethane, at 8.90 μ in 2-cyclohexyloctane, and at 8.88 μ in 9-cyclohexylheptadecane.

8.67 μ . This band, which is broader than the phenyl band at 8.65 μ , is found in all of the cyclohexyleicosanes except 1-cyclohexyleicosane. As it lies close to a band found to be characteristic of 2-methylparaffins, it may be ascribed to a bending of the single tertiary C—H bond.

Paraffin Chain Vibrations

12.75 μ . A broad shoulder in the cyclohexyleicosanes and in the higher normal paraffins. Not observed in the phenyleicosanes where it appears to be masked by the strong broad phenyl band at 13.16 μ .

11.22 μ . Masked by a stronger band in the cyclohexyleicosanes and in 3-phenyleicosane.

7.25 μ . The intensity of this strong, sharp band is greatly depressed in 1-phenyl- and 1-cyclohexyleicosane and in other compounds having rings attached to the end of a chain. This indicates that the band is characteristic of a methyl group.

6.86 μ . The absorption maximum is shifted to 6.89 μ in the cyclohexyleicosanes.

4.43 μ . Shifted to 4.47 μ in the cyclohexyleicosanes.

4.28 μ . See Phenyl Vibrations.

3.83 μ . A weak band which is enhanced as the phenyl or cyclohexyl ring moves toward the middle of the paraffin chain. In normal paraffins the weak band in this position fades into an unresolved shoulder as the length of the chain increases.

2.74 μ . See Phenyl Vibrations.

2.43 μ . See Phenyl Vibrations.

It is sometimes possible to give more detailed information about the origin of a band than is contained in the classification given in Table XV. Thus, some bands may be associated with a terminal $-\text{CH}_3$ group or with the carbon skeleton of a ring or a chain, or they may be designated as C—H stretching, C—H bending vibrations, and so on. Because the data presented here do not add substantially to the basis for a more detailed description of the vibrations associated with the observed band, no description is given here.

COMPARISON OF SPECTRA OF COMPOUNDS WITHIN A SERIES

The preceding discussion has dealt with absorption maxima which occur throughout at least one of the two series of compounds under consideration. Such bands may be applied to determine the general type of compounds for which they are characteristic. Absorption maxima which are characteristic of individual members of a series, or which vary appreciably in position, intensity, or shape, from compound to compound may be used to identify individual compounds.

Phenyleicosanes. Fairly pronounced differences exist between the infrared absorption spectra of individual phenyleicosanes in which the phenyl ring is attached near the end of the *n*-eicosane chain. As the phenyl group moves toward the middle of the chain the differences become much smaller, making differentiation between individual isomers difficult. The greatest differences are found between 7 and 12 μ , where various skeletal vibrations occur, as well as C—H deformation vibrations.

A striking characteristic of the 1-phenyleicosane spectrum is the low intensity of the band at 7.25 μ . With a cell thickness of 0.04 mm., the per cent transmittance for 1-phenyleicosane is 74, whereas the other phenyleicosanes have a transmittance around 50%. Similarly, with a cell thickness of 0.014 mm., *n*-butylbenzene and *n*-hexylbenzene have the transmittance 70% at 7.25 μ , whereas the transmittance for 2-phenyloctane is 50%.

Another characteristic of 1-phenyleicosane, and of other compounds with a phenyl ring attached to the first carbon atom in a chain, is the shift of the 13.16 μ band to 13.42 μ . A smaller shift is observed in the 14.29 μ band which occurs at 14.34 μ in 1-phenyleicosane, or very nearly in the same position as in ethyl-, *n*-propyl-, and *n*-butylbenzene.

A pair of absorption maxima of medium intensity, at 9.19 and 9.32 μ , is characteristic of 2-phenyleicosane. A similar pair of bands is found in 2-phenyloctane at 9.18 and 9.33 μ . As the phenyl ring moves to the middle of the *n*-eicosane chain, the maximum at the shorter wave length decreases in intensity and moves to still shorter wave lengths. A broad shoulder at 9.83 μ is also characteristic of 2-phenyleicosane, as well as of 2-phenyloctane. Less conspicuous is a slight increase in sharpness and intensity of the band at 11.05 μ .

The shifting of the 11.06 μ band, which is in this position for all the other phenyleicosanes, to 11.14 μ is the most distinctive characteristic of 3-phenyleicosane. The maxima at 9.17 and 9.37 μ may also be useful for identifying this isomer.

5-Phenyleicosane has a broad band at 10.67 μ which does not appear in the spectra of the other isomers and is sufficient to distinguish it from them.

The spectra of 4-, 7- and 9-phenyleicosane are almost identical. Only the short wave-length maxima of the 9 μ doublet differ in 4- and 9-phenyleicosane, lying at 9.02 μ in the former and at 8.93 μ in the latter isomer. The 7- and 9-phenyleicosane spectra differ slightly between 9.3 and 10.3 μ . The bands at 9.34 and 9.71 μ are of equal intensity in 7-phenyleicosane, while in 9-phenyleicosane the band at 9.32 μ is less intense than the 9.70 μ band. In 7-phenyleicosane the bands at 10.05 and 10.23 μ are more intense than the corresponding bands in 9-phenyleicosane. Similar differences occur between the spectra of 7-phenyltridecane and 9-phenylheptadecane.

Cyclohexyleicosanes. Spectra of only four other normal paraffins with cyclohexyl substitution were available, and of these the spectra of methyl- and ethylcyclohexane are not very useful for comparison because of the shortness of the alkyl chain.

The differences between the infrared spectra of the seven cyclohexyleicosanes are even less pronounced than for the phenyleicosanes. As in the case of 1-phenyleicosane, a striking characteristic of 1-cyclohexyleicosane is the low intensity of the band at 7.24 μ . Slight peculiarities occur in three other bands. At 8.57 μ 1-cyclohexyleicosane has a broad shoulder, while the other isomers have a sharp absorption maximum between 8.65 and 8.69 μ . The intensity of the band at 11.85 μ is enhanced in 1-cyclohexyleicosane, as is the sharpness of this band and the band at 10.42 μ .

2-Cyclohexyleicosane has several bands not found in the other isomers. A weak band occurs at 10.00 μ with a broad shoulder at 10.11 μ . A band of about equal intensity with a broad shoulder is found at 11.72 μ . Another band, considerably weaker, appears at 10.61 μ . The spectrum of 2-cyclohexyloctane has three bands and two shoulders at these same wave lengths, showing that their occurrence is indicative of a cyclohexyl ring attached to the second carbon atom of a normal paraffin chain. Less conspicuous is the enhancement of the 8.65 μ band in 2-cyclohexyleicosane. This phenomenon is also observed in 2-cyclohexyloctane.

3-Cyclohexyleicosane has one band, a sharp maximum at 12.53 μ , which is not found in any of the other cyclohexyleicosanes. All isomers have a faint band at 9.71 μ , but in 3-cyclohexyleicosane this is exceptionally strong and broad. Some of the isomers have a faint maximum or shoulder at 10.46 μ , which also is broader and stronger in 3-cyclohexyleicosane. A band which occurs at 10.95 μ in 1- and 2-cyclohexyleicosane shifts to longer wave lengths and fades into the broad 11.22 μ -band as the cyclohexyl ring moves toward the middle of the normal paraffin chain. However, in 3-cyclohexyleicosane this band is shifted to 10.90 μ .

The spectra of 4-, 5-, 7-, and 9-cyclohexyleicosane are very nearly alike and have few features to distinguish one from another. The shoulder at 13.62 μ is more intense in 4-cyclohexyleicosane than in the other members of the series. This isomer is also distinguished by a faint maximum at 9.63 μ .

All isomers, except 3- and 5-cyclohexyleicosane, have the strongest maximum in the 9.0-9.5 μ bands at approximately 9.29 μ . The maximum is at 9.245 μ for 3-cyclohexyleicosane and at 9.23 μ for 5-cyclohexyleicosane. The latter isomer is the only one to have a band at 11.60 μ . 7-Cyclohexyleicosane is the only member of the series which has an absorption maximum at 12.73 μ , although a few of the isomers have broad shoulders near this wave length. 9-Cyclohexyleicosane has a sharp maximum at 8.96 μ which is equal in intensity to the 8.88 μ band. Moreover, this isomer has a broad shoulder at about 11.42 μ , which is also conspicuous in 9-cyclohexylheptadecane.

CONCLUDING REMARKS

It has not been an object of the present work to determine the purity of the compounds investigated. To do so would have required a detailed consideration of the method by which each compound was synthesized and of the impurities likely to occur in it, as well as observation of the absorption spectrum of each compound at different stages of purification. Although the results obtained in comparing the various spectra with one another and with the spectra of related compounds indicate that the purity is high, it would not be surprising if one or more of the weaker absorption maxima observed should be found to have been caused by impurities. Nevertheless, the spectra presented here should be adequate for estimating the possibilities and limita-

tions of the application of infrared spectroscopy to the identification of phenyl- and cyclohexyleicosanes and to the analysis of mixtures containing these compounds.

ACKNOWLEDGMENTS

The writers wish to acknowledge their indebtedness to the American Petroleum Institute, and to the late F. C. Whitmore and R. W. Schiessler of Pennsylvania State College, for the loan of the hydrocarbons. One of the authors (K. S.) wishes to express her gratitude to the Ethyl Corporation for the grant of a fellowship.

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Infrared Absorption of Aqueous Solutions of Organic Acids and Their Salts

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The observation of aqueous solutions, hitherto considered difficult, in infrared spectroscopy is discussed. The techniques involving both water and deuterium oxide solutions at various proton or deuterium concentrations are illustrated. The utility of aqueous solution infrared spectroscopy is shown in the cases of carboxylic and amino acids and their metallic salts. An important aid in the identification of carboxylic acid salts and dipolar ion amino acids is proposed.

ONE of the widespread misconceptions concerning the application of infrared spectrometry in organic analysis is that it is impossible or at least difficult to obtain spectra of aqueous solutions. On the contrary, it is often of extreme value to observe spectra in aqueous solution, at various hydrogen ion concentrations, especially in the case of carboxylic acid salts and amino acids (3-12). These salts and amino acids are often the end products obtained by the organic chemist or biochemist in the investigation of both synthetic and natural products, and their identification by infrared spectrometric methods has several advantages over the usual mixed melting point techniques.

The determination of a mixed melting point is dependent upon at least two factors: (1) the possession by the sample of a definite melting point and (2) the possession at the moment by the chemist of a known material to be mixed with the unknown.

Unfortunately, many carboxylic salts do not possess sharp melting points and many chemists do not, at a given moment, possess samples of materials to be mixed with unknowns. The advantages of an infrared spectrometric identification of an unknown over that afforded by the melting point method appear obvious when it is remembered that the spectrogram is an invariant characteristic physical property of the molecule which does not need

to have been obtained at the same time as the spectrogram of an unknown material. Furthermore, the techniques used in obtaining spectra are such that it is not necessary for the molecule to possess a definite melting point; in fact, it is sometimes easier to handle samples in an amorphous than in a crystalline state. Samples containing sufficient amounts of impurities to render melting point determinations useless often will give excellent infrared spectra.

These advantages of infrared identification, especially in the case of only water-soluble salts, are extended when it is realized that aqueous solution techniques are not prohibited.

EXPERIMENTAL

Cells. It is, of course, difficult to use the rock-salt or halite cell windows customarily used in infrared investigations when aqueous solutions are to be investigated. Furthermore, at present, no satisfactory water-impervious coating materials have been found which would permit the use of the usual halite cells. Accordingly, it is necessary to use some of the water-insoluble infrared transparent materials, such as special glasses, fluorite, silver chloride, or perhaps lead chloride, for the fabrication of the cells. Eastman Kodak Glass-25 may be successfully used as cell windows from the visible region out to 5 microns, where the transmittance of two 2-mm. windows may be only 25%.

Fluorite, calcium fluoride, either synthetic or natural, is useful in window thicknesses from the visible region out to about 9 microns.

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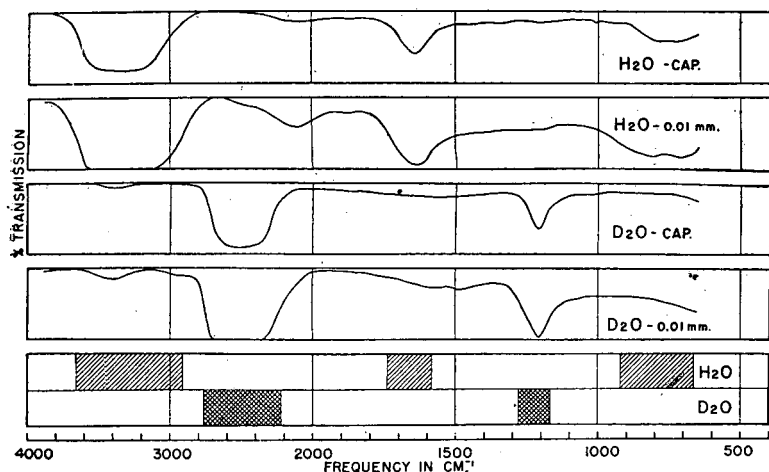


Figure 1. Infrared Spectra of Liquid Water and Deuterium Oxide

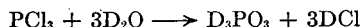
Silver chloride windows are useful throughout the rock-salt and potassium bromide regions but are difficult to handle because of their ductility and chemical reactivity. It is difficult to construct cells of known thickness using silver chloride. In spite of these drawbacks, silver chloride windows are used with silver spacers to obtain the spectra of the aqueous solutions shown in this paper.

Lead chloride windows could be useful in spite of their solubility but are not commercially available at present.

Solvents. The water used is merely a good grade of distilled water without any special treatment or storage. The impurities present are usually of such nature and amount as to exhibit no infrared spectrum.

The deuterium oxide is Stuart Oxygen Company's prewar 99.5% D₂O. The bulk supply has been divided into 1-ml. lots and sealed in Pyrex tubes which are broken and used as needed. After a determination the unused deuterium oxide is placed in a tightly closed container in a desiccator over fresh phosphorus pentoxide until it is again needed.

The deuterium chloride is prepared by distillation from the following reaction mixture:



The sodium hydroxide-*d* is prepared by merely allowing carefully dried sodium to react with deuterium oxide.

INSTRUMENTAL

The spectra were obtained in the open laboratory at 75° F. and 35% relative humidity on a Model 12A Perkin-Elmer spectrometer with electronic direct current amplification feeding into a Brown Elektronik recorder. No special precautions to prevent atmospheric exchange were taken during the preparation of the samples or the recording of the spectra. The mineral oil (Nujol) mulls were prepared in the usual manner using rock-salt plates.

RESULTS AND DISCUSSION

As is well known, liquid water (H₂O) possesses strong infrared absorption near 3300, 1640, and 800 cm.⁻¹ (1, 2), as well as several other weaker absorption bands.

The presence of these intense bands means that little use of water solutions can be made in these regions. This is particularly unfortunate in the case of the 1640 cm.⁻¹ deformation vibration, because it occurs in the center of the extremely interesting and useful X = Y (X, Y = C, O, N) region.

It is possible to shift this angular vibration from 1640 to 1210 cm.⁻¹ by replacing the hydrogen atoms with deuterium. At the same time the 3300 cm.⁻¹, O-H stretching vibration is shifted to 2500 cm.⁻¹ leaving the OH and NH vibrations free of

the solvent absorption. It is therefore possible through the use of two separate preparations using water and deuterium oxide as the solvents to cover the complete rock-salt infrared region.

The spectra of water and deuterium oxide at two thicknesses are shown in Figure 1.

EXCHANGE

When studying molecules in deuterium oxide solution it is well to keep in mind the possibilities of exchange between the deuterium in the deuterium oxide and any active hydrogen atoms that may be present in the molecule. Many molecules containing NH or OH radicals will undergo rapid exchange. This molecular change, however, is of little consequence when the major interest in the spectrum is centered in the double bond region such as in the case of the carboxylic acids, their salts, and the amino acids.

It is readily possible to measure the rate of exchange through the observation of the appearance or disappearance of an absorption band. The activity of the methyl hydrogen atoms of toluene is increased by the substitution of a nitro radical in the para position, giving a rate of exchange slow enough to be

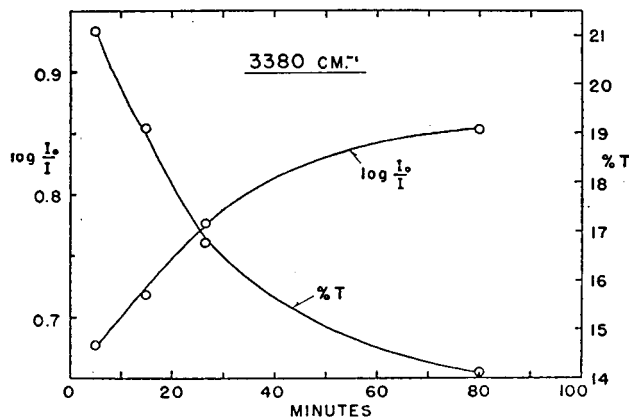


Figure 2. Deuterium-Hydrogen Exchange in *p*-Nitrotoluene

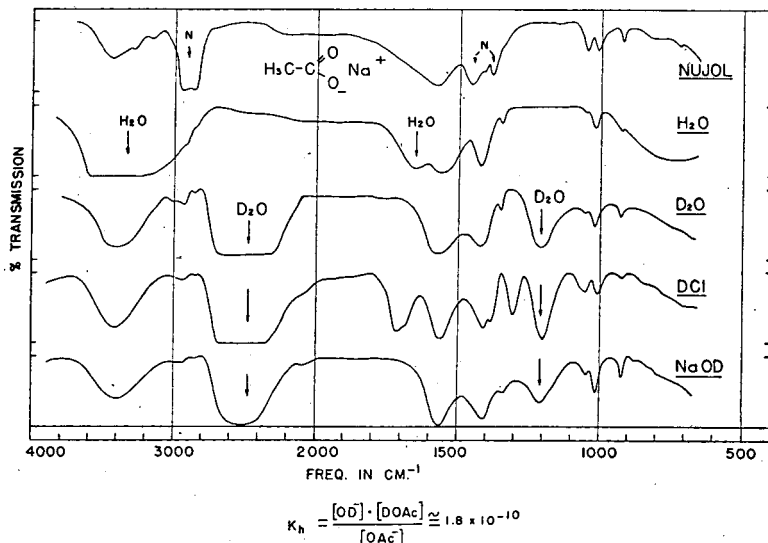


Figure 3. Infrared Spectra of Sodium Acetate

$$K_h = \frac{[OD] \cdot [OAc]}{[OAc]} \approx 1.8 \times 10^{-10}$$

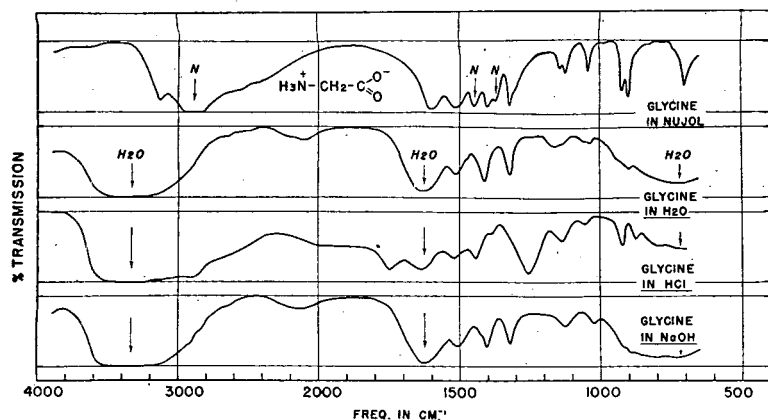


Figure 4. Infrared Spectra of Glycine

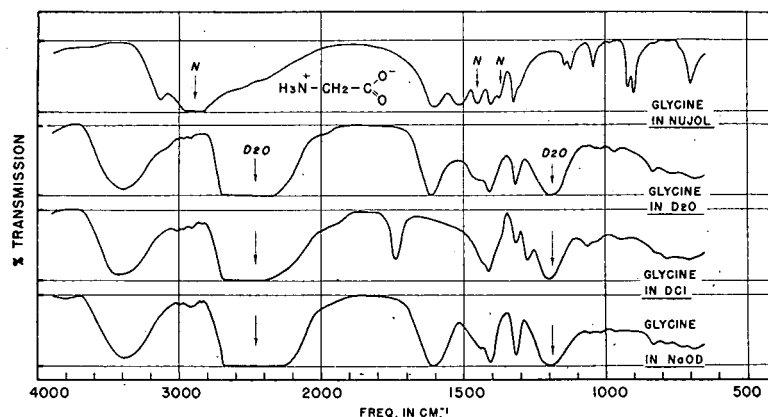


Figure 5. Infrared Spectra of Glycine

measured at reasonable time intervals with the usual infrared recorder system. The optical density, $\log I_0/I$, or absorbance at 3380 cm^{-1} , the O—H stretching vibration, may be measured over an interval of time. Such a curve, including the per cent transmittance curve, is shown in Figure 2 to illustrate the applicability of the method. In many cases the rate of exchange between hydrogen and deuterium is low enough to afford no interference in the short interval of time necessary to obtain an infrared spectrum.

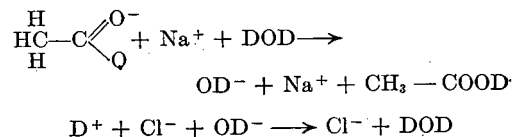
SALTS OF CARBOXYLIC ACIDS

A comparison of the spectra of sodium acetate in white mineral oil, in water, and in deuterium oxide is shown in Figure 3. The C—H stretching and bending vibrations near 2900 and 1375 cm^{-1} , which are obscured somewhat by the CH absorption of the oil, are easily observed in the aqueous solutions. The asymmetrical and symmetrical stretching vibrations of the ionized carboxyl group near 1560 and 1410 cm^{-1} , respectively, are more evident in the aqueous solutions.

The effect of changing the pH (or more properly the pD) of the solutions is also shown in Figure 3. When deuterium chloride in deuterium oxide is used as the solvent, the carbonyl absorption at 1560 cm^{-1} may be made to reduce considerably and a new band near 1730 cm^{-1} appears. The carbonyl radical, whether found in aldehydes, ketones, acids, esters, or amides, usually absorbs near 1735 cm^{-1} , provided there is no disturbing influence such as hydrogen bonding, association, dimerization, conjugation, or strain transmitted from a ring system. The appearance of this 1735

cm^{-1} absorption band may then be attributed to the production in solution of un-ionized, only slightly bonded, carboxyl radicals.

A consideration of the reactions involved



gives a clear explanation of what is happening. Perhaps this may be seen best by considering the hydrolysis constant

$$K_h = \frac{[\text{OD}^-] \times [\text{DOAc}]}{[\text{OAc}^-]} = \frac{K_{\text{D}_2\text{O}}}{K_{\text{acid}}} = \frac{0.33 \times 10^{-14}}{1.8 \times 10^{-5}} = 1.83 \times 10^{-10}$$

When D^+ ions are added $[\text{OD}^-]$ is reduced, forming slightly ionized deuterium oxide and acetic acid-*d* is formed at the expense of the ionized acetate radical $[\text{OAc}^-]$. Consequently, the concentration of acetic acid-*d* is increased sufficiently to appear in the deuterium chloride spectrum of Figure 3.

When a deuteron acceptor, such as the OD^- ion from sodium hydroxide-*d*, is added to the sodium acetate, the spectrum, Figure 3, reverts back to that exhibited by the acetate in deuterium oxide alone with perhaps even less indication of 1725 cm^{-1} absorption.

IDENTIFICATION OF CARBOXYLIC SALTS

This shift of the carbonyl absorption up to 1730 cm^{-1} on the addition of deuterium oxide-deuterium chloride solution to a carboxylic salt is a useful technique for aid in its identification or the detection of its presence in a complex mixture.

AMINO ACIDS

Aqueous phase infrared spectroscopy is useful in connection with studies on amino acids and their salts.

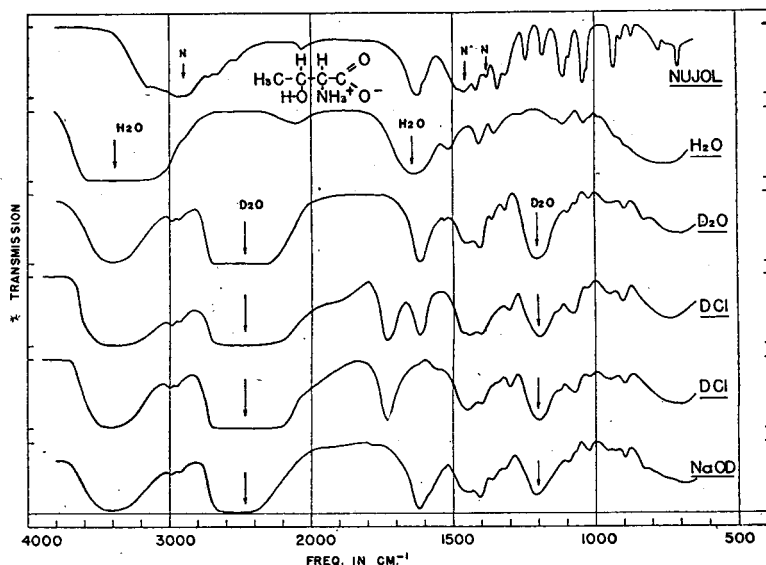
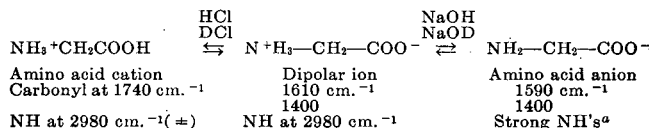


Figure 6. Infrared Spectra of DL-Threonine

The spectra of glycine in oil, water, hydrochloric acid solution, and sodium hydroxide solution are shown in Figure 4. A comparison of these spectra shows that even in spite of the strong 1640 cm^{-1} water bending vibration it is possible to obtain spectra that indicate changes in the molecule with changes in hydrogen ion concentration. The Nujol spectrum indicates that crystalline glycine is either a dimerized acid, from the 1600 cm^{-1} carbonyl vibration, or in the dipolar ion form (*Zwitterion*). That this latter condition prevails is indicated by the type of N—H absorption near 3050 cm^{-1} which is not characteristic of the NH_2 radical. The lack of absorption over 1700 cm^{-1} in the case of the water solution spectrum indicates that solution changes this condition only slightly.

When glycine is put into the hydrochloric acid solution, however, a new band near 1730 cm^{-1} appears along with another strong band near 1250 cm^{-1} . The basic solution reverts to the spectrum of the aqueous solution. A consideration of the equilibria involved is interesting.



^a The N—H stretching vibrations are typical of NH and NH_2 radicals if observed quickly, but are rapidly obscured by the formation of OH groups through exchange between the hydrogen and deuterium atoms.

The observations on the N—H frequencies are somewhat obscured by the OH of the water.

The spectra of glycine in deuterium oxide, deuterium chloride, and sodium hydroxide-*d* are shown in Figure 5. The shift of the 1640 cm^{-1} water band to 1210 cm^{-1} clarifies the carbonyl region. The similarity of the crystalline, aqueous, and amino acid anion (NaOD) phase carbonyls is immediately observable. The shift of this carbonyl to 1730 cm^{-1} is striking in the case of the cation phase (DCl): A new band appears near 1280 cm^{-1} which could correspond to the strong 1250 cm^{-1} band found in the hydrogen chloride spectrum. Inasmuch as the major difference between the crystalline and cation phases is the presence of an OH radical, it is conceivable that this band near 1250 cm^{-1} is associated with the long unassigned C—OH bending vibration or the C—O stretching vibration enhanced by the unsaturation of the carbon atom.

The spectra of DL-threonine are shown in Figure 6. Again, it is evident that crystalline and dissolved threonine exist in the dipolar ion state. The first deuterium chloride spectrum, because of the presence of the two carbonyl bands near 1600 and 1730 cm^{-1} , indicates that the pD (pH) was not low enough to change all of the dipolar ion threonine into the cation state. The second deuterium chloride spectrum shows the effect of adding enough deuterium chloride to the preparation to change most of the threonine to this cationic condition. The change in the intensity of the 1400 cm^{-1} asymmetric $\text{C}-\text{O}^-$ stretching frequency corresponding to the change in the 1600 cm^{-1} band is observable in these two deuterium chloride spectra but it is not so pronounced as in the case of the 1600 cm^{-1} band. The band near 1290 or 1090 cm^{-1} may correspond to the 1280 cm^{-1} band in glycine.

AMINO ACID IDENTIFICATION

This shift of the carbonyl absorption bands on the addition of deuterium chloride and sodium

hydroxide-*d* has proved to be a useful aid in the identification of amino acids.

AMINO ACID SALTS

Inasmuch as samples of amino acids are often obtained in the salt condition, it was thought worth while to examine the spectra of some amino acid salts.

The spectra of glycine and its sodium salt in oil and the sodium salt in deuterium oxide-deuterium chloride are shown in Figure 7. These again illustrate the possibility of using aqueous phase infrared spectroscopy. Unfortunately, the pD was not lowered sufficiently by the addition of sufficient deuterium chloride in the case of the deuterium chloride spectrum to produce the characteristic carbonyl shift to 1730 cm^{-1} . This illustrates, however, the necessity of making certain that the pD has been lowered sufficiently.

The spectra of the sodium salt of DL-alanine run as a smear without Nujol, and in water, deuterium oxide, deuterium chloride, and sodium hydroxide-*d* are shown in Figure 8. Again in the case of the deuterium chloride solution the shift of the carbonyl from 1600 to 1730 cm^{-1} is evident along with changes near 1400 and 1290 cm^{-1} . As can be readily observed, the concentration of the ionized carboxyl has not been sufficiently repressed to cause the disappearance of the 1600 cm^{-1} band at the expense of the 1730 cm^{-1} absorption.

CONCLUSIONS

Aqueous phase infrared spectroscopy is a practicable technique which will permit the observation of the complete rock-salt spectrum if both water and deuterium oxide are used.

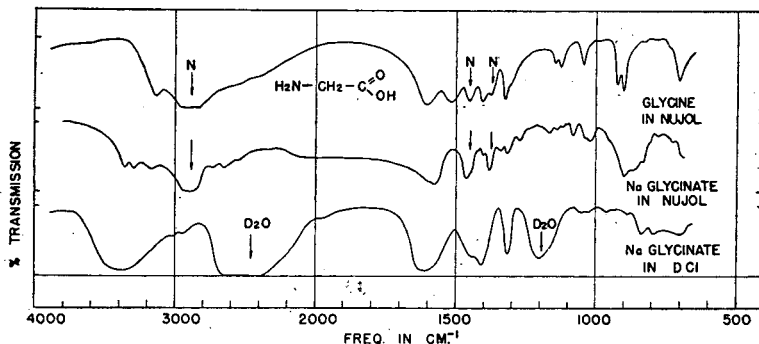


Figure 7. Infrared Spectra of Glycine and Sodium Salt

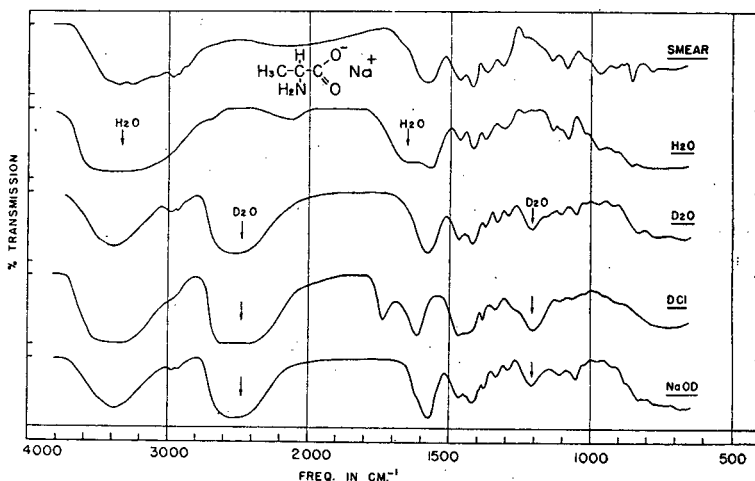


Figure 8. Infrared Spectra of DL-Alanine, Sodium Salt

Deuterium oxide solutions are especially useful in observing carbonyl frequencies.

Exchange, which may be measured by infrared methods, between the air and the sample and the deuterium oxide is not troublesome.

Carboxylic acid salts, often insoluble in other solvents, may be observed in water and deuterium oxide solutions.

The addition of deuterium chloride to a carboxylic acid salt produces a shift in the carbonyl absorption from 1600 to 1730 cm.^{-1} which is useful in the identification of such salts.

Amino acids and their salts may be studied by aqueous phase infrared methods.

Amino acids may be changed from the dipolar ion form to the cation and anion form with attendant changes in their infrared spectra.

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ELEMENTARY ISOTOPIC ANALYSIS

Determination of Oxygen, Carbon, and Nitrogen in Organic Compounds

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The determination of oxygen, carbon, and nitrogen in organic compounds by means of elementary isotopic analysis consists in the addition of known amounts of the heavy isotope of these elements (diluted or pure) to a known amount of the substance to be analyzed and the determination of the isotopic ratio by means of the mass-spectrometer after equilibration. The amount of element sought follows from the simple mixture rule. The method does not require quantitative determinations or specificity of reaction. Thus, possibilities of precision analysis are afforded in new fields.

ISOTOPES have not, as yet, been used in elementary or ultimate analysis. Their ever-increasing availability and the development of the precision mass spectrometer as a routine laboratory instrument offer the analytical chemist a powerful new tool. The use of heavy isotopes of oxygen, carbon, and nitrogen for elementary analysis is described in this paper. Brief preliminary notes have appeared previously (1, 2, 5).

PRINCIPLE AND ADVANTAGES OF ISOTOPIC METHOD

In classical chemical analysis, the element or compound to be determined must show some reaction which is specific for that constituent, at least in so far as the other components of the system are concerned. Generally three steps are followed, and in each stage all handling must be quantitative. The constituent sought must be concentrated, and free of most or all of the other constituents of the mixture; it must then be converted into some chemically pure compound, but not necessarily of a definite composition, and isolated from the remainder of the constituents; and this pure compound is then usually converted into some other compound of known and constant composition, and determined in this form.

Two widely differing types of analysis may be used to illustrate these points:

In the analysis for, say, iron in a complex silicate mixture, the iron is first quantitatively separated, together with varying amounts of aluminum, titanium, etc., then quantitatively isolated as chemically pure hydroxide or sulfide, and, finally, again quan-

titatively, converted to the oxide, Fe_2O_3 , and weighed as such. Similarly, in the usual Liebig-type determination of carbon in organic materials, the carbon is first quantitatively converted to carbon dioxide, which is then separated from other components of the system (water, nitrogen, etc.) and then quantitatively converted to carbonate and determined by weighing.

To some measure, the methods of volumetric analysis have considerably simplified the task of the analyst. Thus, in some cases, the second and third steps may be by-passed, or essentially eliminated by titration with standard solutions. Nevertheless, there is still the same feature present as in gravimetric analysis—the considerable number of operations required must all be performed quantitatively.

In elementary isotopic analysis, specificity of reaction or any quantitative determination is not required. The only requirements of the isotopic analyst for a quantitative procedure lie in weighing out the sample and in measuring the volume of the added isotope. The isotope ratio in the gas sample after reaction is determined by the mass spectroscopist. Thus actually, the only operations the isotopic analyst must perform are trivial ones from the standpoint of a classical analyst: to mix his sample well with the added isotope, equilibrate it by heating, and take a representative sample of the reaction products. These operations require no analytical skill—they do not require the analyst to devise a method that will work quantitatively and then actually carry it out with accuracy and precision.

Both stable and radioactive isotopes may be used as analytical tracers. However, because stable isotopes, especially those forming gaseous compounds, can be determined with greater accuracy and convenience by modern mass spectrometers than radioisotopes, the authors have first used the stable isotopes.

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The main elements of organic chemistry—oxygen, carbon, nitrogen, and hydrogen—are of particular importance and the determination of the first three is discussed here. A later paper will discuss the extension of the method to the determination of other elements, particularly hydrogen and sulfur.

ANALYTICAL FORMULA AND EXPERIMENTAL FOUNDATION

The procedure is a very simple adaptation of the isotope dilution principle originally introduced by Hevesy and Paneth (3) in 1913 by means of the naturally radioactive isotopes of lead. In order to equilibrate the "organogens" (the main elements of organic chemistry)—that is, reach equal distribution of the isotopes of any particular element among its various compounds present—it is necessary to heat the components to a temperature above red heat, in some cases, preferably in the presence of a catalyst, for less than one hour. After isotopic equilibrium is established, the mixture is rapidly cooled, thus "freezing" the high temperature equilibrium.

If a known weight of the sample, a , containing x weight % of the element to be analyzed, is equilibrated with a known weight, b , of a labeled element, containing $m\%$ of it in excess of the normal isotopic concentration and if $n\%$ is the excess isotope concentration after equilibration, it follows from the simple mixture rule that

$$x\% = \frac{b(m - n)}{an} \times 100 \quad (1)$$

Because the isotopes are mixed and measured on an atom per atom basis, b should be expressed either in gram-atoms or, more simply, in weight units using the same atomic weight of the element as in a . Thus, in Equation 1, b is not expressed in actual milligrams of the heavy isotope, but in equivalent milligrams of the normal isotopic mixture. In other words, the volume of gaseous isotope added is converted into weight units by using the normal atomic weight of the element—i.e., the same as in a , and not the actual atomic weight of b . A complete mathematical treatment of the isotope dilution method is given by Kamen (4).

Isotopic equilibrium was essentially attained in all cases investigated by the authors, by heating the components to 600° to 800° C. for 0.5 to 1 hour. However, attainment of complete equilibrium is not a requirement of the method. It is not necessary to attain it if the equilibrium ratio can be calculated from other mass spectroscopic data.

The following experiment indicates the attainment of equilibrium in the case of oxygen.

Oxygen Equilibration. In this experiment 0.368 millimole (8.24 cc. at N.T.P.) of carbon dioxide plus 1.66 millimoles (29.9 mg.) of water, both of 0.20 atomic % O^{18} , was heated at 700° C. for 30 minutes in an 80-cc. platinum tube with 0.674 millimole (15.10 cc.) of oxygen of 1.22 atomic % O^{18} . Based on the carbon dioxide peak, the final mixture contained 0.58 atomic % O^{18} ; the calculated value at equilibrium should be 0.57 atomic % O^{18} .

Taking into consideration the accuracy of the mass spectrometer determinations in this range, it is safe to assume that equilibrium was reached.

At the equilibration temperatures used the isotopic distribution among the various compounds present is not what would be expected from classical considerations in all cases. However any possible deviation from classical distribution is so small that it is beyond the detecting power of the mass spectrometer. In the future, when greater accuracy will be possible, the deviation of the equilibrium constant from classical behavior may be taken into consideration, where necessary. More rapid and efficient freezing of the equilibrium could also be achieved if desirable.

In determining any element it is usually not necessary to accomplish a quantitative reaction—for example, in the determination of oxygen in organic compounds complete combustion is not necessary. Data illustrating this point are shown in Table II.

Analyses 1 and 2 show the determination of oxygen in formic acid, using in analysis 1 oxygen sufficient for complete combustion, and in analysis 2 oxygen insufficient for complete combustion. Even in the presence of products such as methane and carbon

Table I. Precision of Spectrometer Values of Three Identical Samples Each Scanned Three Times

(Consolidated Engineering Corporation mass spectrometer)		
Sample No.	Scan No.	% C^{13}
1	1	5.38
	2	5.42
	3	5.42
2	1	5.37
	2	5.42
	3	5.33
3	1	5.40
	2	5.40
	3	5.38
		Av. 5.393 ± 0.025

monoxide, the experimental values indicate that the oxygen of the sample is completely equilibrated among the various oxygen compounds present. When oxygen is used in excess, the oxygen peaks—i.e., O_2^{16} and $O^{18}O^{18}$ —may be used to calculate the isotopic ratio (the O_2^{18} peak is generally too small to measure). The authors prefer to use the carbon dioxide peaks of $C^{12}O_2^{16}$ and $C^{12}O^{18}O^{18}$ for determining the isotope ratio, as more reliable figures are obtained from them. They used the mass spectrometer of the Consolidated Engineering Corporation, Pasadena, Calif., with automatic recording, for their measurements.

As $(m - n)$ and n enter into the equation, accuracy is highest when the amount of isotopically labeled element b approximately equals the element content of the sample, $a \times x$. [A detailed discussion of errors in the isotope dilution technique is given by Rittenberg and Foster (8).] In the oxygen analyses, the spread between the normal concentration of O^{18} and that of the isotopic sample is about 1.0 atom %. Hence, accuracy cannot be much better than about ±3% of the oxygen content of the sample. Using C^{13} of concentration 10 to 15 atom % above normal, accuracy of perhaps 0.2 to 0.3% of the carbon content present should be possible. In general, the authors have reached somewhat lower accuracy than this, as their mass spectrometer determinations show an average precision of about ±0.5 to 1.0% in the isotope ratio in multiple analyses of the same gas mixture. This is shown in Table I, where three identical samples were scanned three times each. In general, the limiting factor in the accuracy results by this method is: (1) the precision of the spectrometer determination of the isotopic ratio, and (2), the isotope concentration. Hence, the absolute accuracy increases with decreasing content of element sought and, inversely, decreases with increasing amount of element sought. The authors expect to use the new Nier isotopic instrument (6) to increase accuracy and precision in measuring the isotope ratio and to work with more concentrated isotopes. A second instrument specially designed for isotopic ratio determinations, has been designed by the Process and Instruments Company, 60 Greenpoint Ave., Brooklyn 22, N. Y. A brief description of this instrument has appeared (7).

APPARATUS FOR ELEMENTARY ISOTOPIC ANALYSIS

Figure 1 is a drawing of the apparatus.

The reaction vessel, D , is of quartz, of 90-cc. volume; for determination of oxygen, platinum vessel of 80-cc. volume is used (the plug, B , is also replaced by a sealed tube of platinum) in order to avoid any possible exchange of oxygen of the sample and tracer with the oxygen of the walls. The tube is joined to the system through a graded seal for the quartz tube; de Khotinsky cement is used with the platinum tube. The center part of the system consists of a capillary glass manifold 1 to 1.5 mm. in inside diameter. The small sample bottle, three measuring burets, two of 50-cc. and one of 10-cc. volume, and 500-cc. storage vessels for $C^{13}O_2$, $N^{15}H_3$, D_2 , and O_2^{18} are attached to it.

The right-hand part of the system is built of glass tubing of the usual size. Small traps, L_1 and L_2 , serve to condense and purify reaction products. U-tube M contains a suitable drying agent, while tube K serves as a by-pass of M and L_2 .

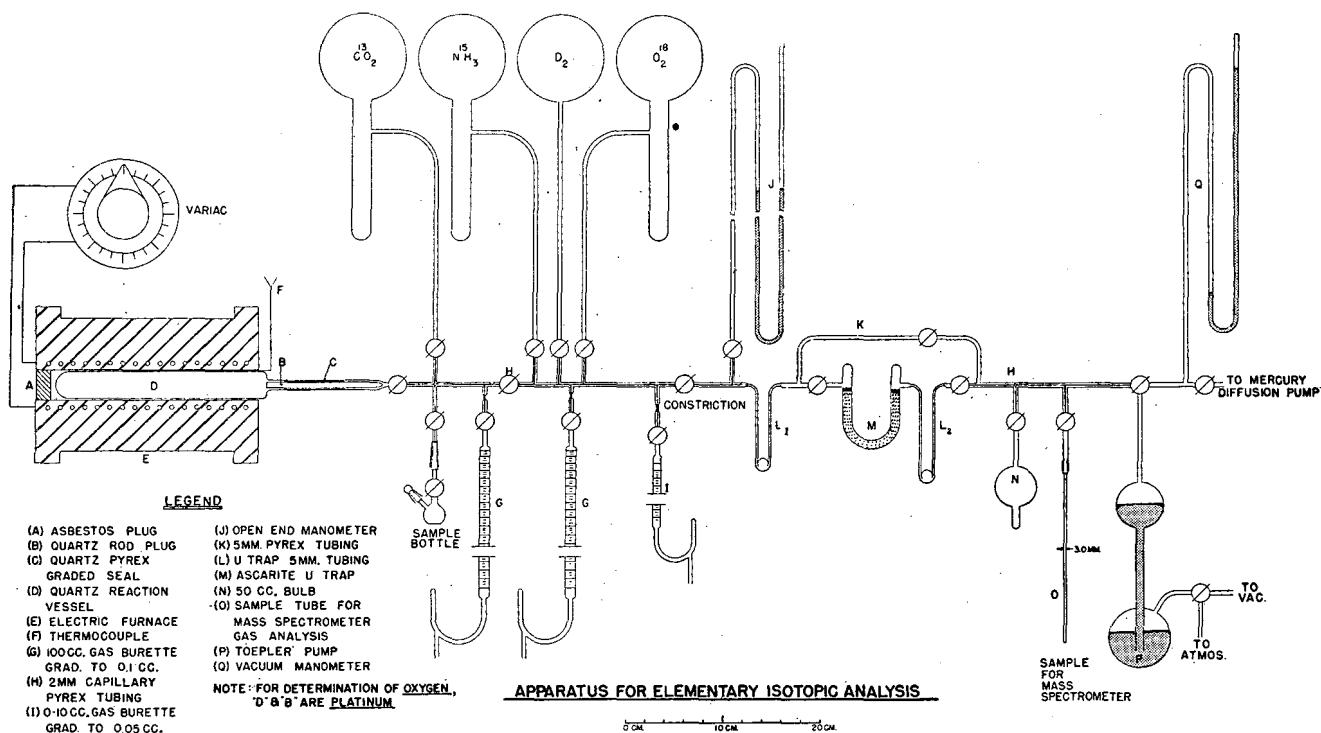


Figure 1

Bulb *N* is used for collecting noncondensable gas, while capillary *O* is used for collecting the mass spectrometer samples. Toeppler pump *P* is available for pumping and compressing. Mercury manometers *J* and *Q* are available for pressure measurements.

ISOTOPES AND PURITY OF SAMPLES

In the determination of oxygen, the heavy isotope was added as oxygen gas, derived from the microelectrolysis of H_2O^{18} . The O^{18} was present in 1.2 atom % as against a normal value of 0.20 atom %. In recent analyses, 10 atom % O^{18} , from the authors' heavy oxygen thermal diffusion column, was used. C^{13}O_2 used was obtained from the combustion of C^{13}H_4 from the thermal diffusion plants. It was purified through precipitation as $\text{BaC}^{13}\text{O}_3$, subsequent regeneration with hydrochloric acid, and further purification by pumping and condensation in a vacuum system. The C^{13} was present in 12.2 atom % concentration; the normal concentration is 1.04%. Nitrogen was used in the form of N^{15}H_3 , derived by reaction of $\text{N}^{15}\text{H}_4\text{NO}_3$ with potassium hydroxide. The N^{15} concentration was from 32 to 35 atom %; the normal concentration is 0.38%. The chemical purity of the final tracer used was checked by mass analysis.

The samples were the purest chemicals obtainable, usually freshly distilled, and only the heart cut was analyzed. In all cases the refractive indexes were determined by means of an Abbé refractometer; they checked the best literature values.

In view of the fact that this procedure is probably most valuable for the determination of oxygen, a detailed description of the technique used will be given for this element only. Similarly, the method of handling the sample to be analyzed, as described in the following section, is applicable only to volatile pure compounds.

DETERMINATION OF OXYGEN

The system is evacuated by a diffusion pump to less than 10^{-4} mm. The liquid sample is placed in the sample bottle and the air above the sample is removed by pumping on the bottle for a few seconds. The weight of the evacuated flask is then taken on a semimicrobalance to ± 0.02 mg. After removing furnace *E* and cooling the end of the vessel in a dry ice bath, by manipulating the proper stopcocks the sample is distilled over into the platinum

reaction vessel. The weight of sample to be distilled over is figured roughly on the basis of the estimated oxygen content; the amount is regulated by taking into consideration the volatility of the sample and the time of distillation. After the desired amount has been taken out, the sample bottle is reweighed. The usual sample size taken is 20 to 40 mg.; heavy oxygen gas (a mixture of O_2^{18} , $\text{O}^{18}\text{O}^{18}$, and O_2^{18}) is then admitted from the buret—the volume used depends on the estimated oxygen content of the sample, for accuracy is highest when the amount of isotopically labeled element added approximately equals the oxygen content of the sample. The volume taken is accurately measured, the barometric pressure and temperature are recorded, the volume is calculated to normal temperature, and the pressure and weight of gas is calculated, based on $\text{O} = 16.0000$ —i.e., 1.0 cc. at N.T.P. = 1.4290 mg. of oxygen. (If the oxygen is not pure approximate corrections are made.)

Table II. Determination of Oxygen

Analysis No.	1		2	3	4	5
	Formic Acid Excess of O_2	Acetic Acid	Deficiency of O_2	Acetic Acid	1-Nitro-ethane	Ethyl Ether
<i>a</i> , mg. of sample	38.2	60.4	26.0	20.9	52.7	
<i>b</i> , mg. of O^{18} gas taken (using atomic wt. of O = 16.0000) (cc. at N.T.P.)	20.0 (14.0)	22.2 (15.5)	36.5 (25.5)	31.4 (22.0)	12.03 (9.4)	
<i>m</i> , atom % O^{18} in <i>b</i> , above normal concentration	1.00	1.00	1.035	1.05	1.07	
<i>n</i> , atom % O^{18} of equilibrated mixture, above normal concentration	0.425	0.345	0.75	0.82	0.57	
<i>x</i> , % oxygen in substance, calculated from Formula 1	70.8	69.8	53.4	40.3	19.8	
% oxygen, theoretical	69.5	69.5	53.3	42.6	21.6	

The tube containing the mixture of the sample and heavy oxygen is then heated in the electric furnace. The latter, which is maintained at about 800°C ., is drawn over the tube, held for 15 minutes, then removed, and the end of the tube is cooled down in liquid nitrogen or with dry ice, for the purpose of pulling back into the reaction zone any fraction of the sample that may have distilled over unchanged into the plugged portion of the tube.

After 5 minutes of cooling, the heating and cooling cycle is repeated. A final, third heating is then given the sample.

The subsequent handling of the sample is such as to isolate the carbon dioxide rapidly because the most reliable values are obtained from the carbon dioxide peaks. The product gas is quickly taken over into the Toepler pump; by-pass *K* is used, thus eliminating U-tube *M*, while trap *L*₁ is immersed in a dry ice bath to remove water and other easily condensable materials.

From the Toepler pump, the product gas is compressed into trap *N*, which is cooled in liquid nitrogen; noncondensable gases are pumped off. After the carbon dioxide formed in the reaction is thus effectively concentrated, trap *N* is warmed to dry ice temperature and the carbon dioxide is taken over into sample tube *O* by way of the Toepler pump. The sample tube is sealed off in three to five sections; two or three are sent for mass spectrometer analyses, and the remaining samples are kept for eventual checking.

Table III. Determination of Carbon

Analysis No.	1	2	3
Substance analyzed		Acetic Acid	Iso-octane
<i>a</i> , mg. of sample	20.47	24.04	20.96
<i>b</i> , mg. of C, added as (CO ₂ + C ¹³ O ₂) (using atomic weight of C = 12.01)	7.90	11.76	11.10
<i>m</i> , atom % C ¹³ in <i>b</i> above normal concentration	11.18	11.20	11.24
C ¹³ O ₂ content of equilibrated mixture, %	6.39	7.19 ₅	5.37 ₀
	6.41	7.19 ₀	5.40 ₀
	6.36	7.20 ₅	5.37 ₅
Av.	6.39 ±	7.197 ±	5.381 ±
	0.02	0.006	0.012
<i>n</i> , average atom % C ¹³ of equilibrated mixture above normal concentration	5.35	6.157	4.341
<i>z</i> , % carbon in substance, calculated from Formula 1	42.1	40.07	83.50
% carbon, theoretical	40.00	40.00	84.19

The presence of nitrogen peaks at masses 28 and 14 (and also the argon mass 40 peak, if nitrogen is present in the compound) indicates air contamination during the determination. Based on the height of these peaks, a quantitative correction for atmospheric oxygen may be applied to the oxygen value. In the authors' work, this correction has usually been less than 3% of the total oxygen value. Typical results are shown in Table II.

Cleaning of Platinum Tube. If an analysis has been run with a deficiency of oxygen, some carbonaceous material may be present in the tube. This is readily removed after analysis by admitting pure oxygen into the tube, heating it in the furnace for a few minutes, and evacuating. This procedure may be repeated once or twice if necessary. A simple and sensitive test for any carbon still present is to watch for a ring of solid carbon dioxide in the liquid nitrogen or air traps *L*₁ or *L*₂, just above the surface of liquid nitrogen. With some practice, a fraction of a milligram of carbon dioxide can thus be detected. It is convenient to clean the platinum tube immediately after an analysis.

Absence of Adsorbed or Chemisorbed Oxygen in Platinum Tube. The following experiment was performed to prove the absence of any combined oxygen in the platinum tube in this method of operation.

The platinum tube was heated to 775° C. in pure ordinary oxygen for 1.5 hours and then evacuated; 3.4 cc. of enriched heavy oxygen were admitted into the tube and heated for 15 minutes at the same temperature. This oxygen was then mass analyzed and compared with the original sample, with the following result:

O¹⁸O¹⁸ before heating = 2.49 ± 0.03% of O₂

O¹⁸O¹⁸ after heating = 2.47 ± 0.03% of O₂

Within experimental error, no change in concentration occurred, proving the absence of oxygen, in any form, in the tube.

DETERMINATION OF CARBON

C¹³O₂ and sufficient oxygen for complete combustion of the sample are admitted to the quartz or platinum vessel, after sample has been added. In this case, because carbon dioxide is

formed quantitatively as a result of combustion, the C¹³O₂ need only be mixed with the carbon dioxide formed; it is not necessary to equilibrate. The gaseous products are then handled exactly as in the case of the analysis for oxygen. Results are shown in Table III.

DETERMINATION OF NITROGEN

In the determination of nitrogen, the quartz or platinum tube may be used. The oxidation of the sample is effected by cupric oxide in the tube, to minimize the possibility of contamination by traces of nitrogen if oxygen were used. The fresh copper formed by the oxidation serves also as the reducing agent for oxides of nitrogen formed. Either iron wire or platinum (plus osmium, if desirable) wire may be used for equilibration of N₂¹⁴, N¹⁴N¹⁵, and N₂¹⁵. However, complete equilibrium between these isotopic molecules is not necessary, as the mass 28, 29, and 30 peaks are all used to calculate the total N¹⁴ and N¹⁵ amounts.

After reaction is complete, the sample is expanded through the Ascarite trap, *M*, to absorb carbon dioxide and water, into the Toepler pump. It is then thoroughly scrubbed, by passage back and forth through *M*, using the Toepler pump and liquid nitrogen around trap *L*₁. Finally, the gas which is neither absorbed by the Ascarite nor condensed by the nitrogen is expanded into the Toepler pump and taken into sample tube *O*.

A correction for air leakage into the system may be made on the basis of the argon mass 40 peak, as in the case of the oxygen analysis. The cupric oxide bed is regenerated by admitting air into the hot tube, thereby converting the reduced copper to the oxide again, and pumping out any excess air. Typical results are shown in Table IV.

Complete equilibration among N₂¹⁴, N¹⁴N¹⁵, and N₂¹⁵ is not necessary, and has not been attained in the authors' analyses. This may be seen by a breakdown of some of the data, as shown in Table V. If the N¹⁵ content of the equilibrium mixture is known, the relative peak heights of the 28, 29, and 30 masses at equilibrium may be calculated; they are shown in per cent of total nitrogen, for several determinations, in the column of Table V labeled "theory." Actual peak heights from spectrograph charts for these runs are shown in the column labeled "Expt.," expressed in per cent. The values are slightly off equilibrium in all cases, mostly in analysis 1. In this case the heating period was only 45 minutes, in contrast to 60 minutes for the others. Longer heating times should permit closer attainment of equilibrium, but this is not necessary.

Table IV. Determination of Nitrogen

Analysis No.	1	2	3	4
Substance analyzed	Pyridine (C ₅ H ₅ N)		Nitroethane (C ₂ H ₅ NO ₂)	
<i>a</i> , mg. of sample	25.56	30.02	25.04	16.97
<i>b</i> , mg. of N ₂ added as (NH ₃ + N ¹⁵ H ₃) (using atomic weight of N = 14.008)	1.79 ₅	4.27	4.43	3.43
actual quantity of labeled NH ₃ added, cc. at N.T.P.	2.33	5.54	5.75	4.45
<i>m</i> , atom % N ¹⁵ in <i>b</i> above normal concentration	34.84	34.84	32.10	32.10
N ¹⁵ content of equilibrated mixture, %	10.52	16.30	16.60	17.55
	10.59	16.18	16.38	17.48
			16.34	17.43
			16.34	17.56
Av.	10.55 ±	16.24 ±	16.41 ±	17.51 ±
	0.04	0.13	0.06	0.05
<i>n</i> , average atom % excess of N ¹⁵ of equilibrated mixture above normal concentration	9.79	15.48	15.65	16.76
<i>z</i> , % nitrogen in substance calculated from Formula 1	17.96 ±	17.79 ±	18.60 ±	18.52 ±
% nitrogen, theoretical	0.09	0.26	0.14	0.13
	17.74	17.74	18.66	18.66

CALCULATION OF RESULTS AND CORRECTION FOR AIR CONTAMINATION

In analysis for oxygen and nitrogen, air contamination must be evaluated. This error may be due to leaks from two sources;

Table V. Actual Peak Height Ratios and Those Calculated Assuming Complete N¹⁴-N¹⁵ Equilibrium

Analysis No. Sample No.	1		2		3		4		5		Δ T-E	
	Theory %	Expt. %	Theory %	Expt. %	Theory %	Expt. %	Theory %	Expt. %	Expt. %	Expt. %		
Mass 28, N ₂ ¹⁴	79.9	82.3	70.0	71.3	69.9	70.8	68.0	68.7	69.0	68.6	68.8	-0.8
Mass 29, N ¹⁴ N ¹⁵	19.0	14.5	27.3	24.6	27.4	25.6	28.9	27.6	27.4	27.6	27.5	+1.4
Mass 30, N ₂ ¹⁵	1.1	3.1	2.7	4.0	2.7	3.5	3.1	3.7	3.7	3.7	3.7	-0.6

(1) the analysis apparatus, or (2) the mass spectrometer. In the oxygen case, it may be subtracted by noting the heights of the nitrogen peaks and applying a correction for air oxygen. In case of nitrogen, the argon peak of mass 40 is used. Though it is simple to construct a completely tight apparatus and to eliminate air leakage into the spectrometer, none the less analyses with as much as 5% air present, as shown by the spectrometer charts, have given good accuracy when the air is corrected for.

A typical calculation of an analysis, including correction for air, is shown in Table VI. It represents sample 3 (out of 5) of nitrogen analyses 4 (see Table IV). Section 1 gives the actual peak heights for three scannings. Section 2 gives the ratio of various peaks for air and carbon dioxide as determined in the mass spectrometer. They are used in section 3 to correct the initial results for air and other possible contaminations. The sample contained about 5% air, but the correction for atmospheric nitrogen can be made without any ambiguity.

Table VI. Sample Calculation of Determination of Nitrogen in Nitroethene

[Analysis No. 4, sample No. 3 (see Table IV)]

1. Mass Spectrometer Values of Peak Heights (3 Scannings)

Scanning	Mass 28 Peak	Mass 29 Peak	Mass 30 Peak	Mass 40 Peak (Argon)	Mass 44 Peak (CO ₂)	% N ¹⁵ (Uncorr.)
1	1080.0	413.0	55.2	0.8	3.0	16.90
2	1026.0	391.0	52.5	0.9	3.0	16.85
3	975.0	375.0	50.0	0.9	3.0	16.95

2. Typical Air and Carbon Dioxide Calibrations of Mass Spectrometer

Nitrogen mass peak 28/argon mass peak 40 =	50.6
Nitrogen mass peak 29/argon mass peak 40 =	0.380
Nitrogen mass peak 30/argon mass peak 40 =	0.000
Mass peak 28, due to CO from CO ₂ peak/CO ₂ mass peak 44 =	0.1145
Carbon dioxide mass peak 44/argon mass peak 40 =	0.125

3. Typical Correction for Scanning 2 of Analysis 4 Above

	Mass 28 Peak (N ₂ ¹⁴)	Mass 29 Peak (N ¹⁴ N ¹⁵)	Mass 30 Peak (N ₂ ¹⁵)	Mass 40 Peak (A)	Mass 44 Peak (CO ₂)
Uncorrected peak height	1026.0	391.0	52.5	0.9	3.0
Corrections for					
Background	-1.9				-1.0
Air	-45.5	-0.4	0	-0.9	-0.1
CO ₂	-0.1	0	0		-1.9
Corrected peak height	978.5	390.6	52.5	0.0	0.0

The % N¹⁵ is then calculated as follows:

$$\% N^{15} = \frac{(\frac{1}{2} \text{ of } 29 \text{ peak}) + (30 \text{ peak})}{(28 \text{ peak} + 29 \text{ peak} + 30 \text{ peak})} \times 100$$

Using the corrected peak heights—i.e., values of the bottom line of Table VI—we obtain:

$$\begin{aligned} \% N^{15} &= \frac{195.3 + 52.5}{978.5 + 390.6 + 52.5} \times 100 \\ &= 17.42\% \end{aligned}$$

By similar corrections for the Nos. 1 and 3 scannings we obtain the corrected average N¹⁵ content:

Scanning	% N ¹⁵	
	Uncorrected	Corrected
1	16.90	17.44
2	16.85	17.42
3	16.95	17.57
	Av. 17.48 ± 0.06	

Thus the figure 17.48 represents the final corrected value of sample No. 3, analysis No. 4, and as such is given in Table IV.

A perusal of Tables II, III, and IV shows substantial agreement with expected results. The accuracy attained is sufficient for general purposes. The simplicity of the method particularly recommends itself, and especially for oxygen the isotopic method has immediate practical value. This method is susceptible to further improvement in accuracy with the use of more highly concentrated isotopes and Nier's precision isotopic mass spectrometer (6).

Assuming accuracy of measurement in the newer isotopic spectrometers to be of the order of 0.2 to 0.3% of the amount present—i.e., 2 to 3 parts per thousand—it would be necessary to use isotopic enrichment only of the order of 50 atom % to take full advantage of the accuracy possible with the method.

HANDLING PROCEDURE FOR GASEOUS AND NONVOLATILE SAMPLES

The authors' way of admitting sample to the reaction vessel may be used only in the case of a volatile pure compound. For gas samples, a buret with a male joint may be inserted in place of the sample bottle and a definite volume taken from it. For analysis of a liquid, the reaction vessel is removed from the system, cooled, and maintained in a vertical position, and the liquid is added, from a weighing buret. Similarly, for analysis of a solid, the sample is weighed in a glass tube containing a solid glass plunger, the tube is inserted into the reaction vessel, and sample is discharged and determined by difference. In either of these latter cases, the vessel is then connected to the remainder of the system either by glass blowing, through a graded seal, or with de Khotinsky cement. Actually, when only the quartz tube is used—i.e., for analyses other than for oxygen—the tube may be maintained permanently in a vertical position and a side arm used for admitting sample.

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Composition of pH-Responsive Glasses

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A review of the facts relative to the composition of pH-responsive glasses is presented. Comparisons of pH glasses can best be made on the basis of mole per cent composition. The performance of a pH-responsive glass is in part dependent on the role of the ionic radii of the modifying atoms within the silicon-oxygen (Si-O₄) network. The stability, sodium errors, etc., should depend considerably on the electrostatic forces prevailing within the interstices of the network.

THIS paper reviews the facts relative to the composition of pH-responsive glasses in order better to understand the mechanism of the glass electrode.

A rather extensive series of papers has presented some theory of the glass electrode (1, 6-9, 13). Glass composition should be closely related to the mechanism of glass pH electrodes. A summary of some of the more important publications on glass composition may serve to indicate what information is still lacking.

Hughes (10) pointed out that composition of the glass has an important influence on the behavior of a Haber type of electrode. He used available commercial glass and gave qualitative pH performance data upon six different compositions, expressed in weight per cent. In Table I for the sake of comparison the equivalent mole per cent composition has been added. Hughes concluded that "a glass containing 72% SiO₂, 8% CaO, and 20% Na₂O proved very satisfactory." In terms of mole per cent this glass is 72.04% silica, 8.57% calcium oxide, and 19.39% sodium oxide.

Elder and Wright (4) employed a glass of nearly the same composition as recommended by Hughes. In a subsequent paper (3) they used five commercial glasses, but gave no data on their composition.

MacInnes and Dole (14) published data on 16 different types of glass as applicable to pH measurements; they expressed all compositions in weight per cent. They did not employ the Haber bulb type of electrode, but utilized their design of thin membrane type of electrode. In Table II the equivalent mole per cent has been added.

They concluded that the best glass consisted of 72% silica, 6% calcium oxide, and 22% sodium oxide; this composition converted to mole per cent is 72.17% silica, 6.44% calcium oxide, and 21.39% sodium oxide. This is a general confirmation of the finding by Hughes. The MacInnes-Dole glass was subsequently manufactured as Corning 015 glass.

The difference in behavior of the glasses studied by MacInnes and Dole is not easily tabulated, because the information was presented in terms only of stability of asymmetry potential, resistance, and initial error in 0.1 N sodium hydroxide for the very thin membranes.

Kahler and De Eds (11) used two glasses of the Corning 015 composition from different sources, and another similar glass containing some aluminum oxide and lead oxide. They did not give systematic data as to the differences.

Table I. Composition of Hughes Glasses

Glass	No. 1, X-Ray		No. 2, Soft German		No. 3 Moncrieff		No. 793A		No. 444		White Flint	
	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %
SiO ₂	66.88	69.22	70.62	72.25	67.56	70.33	71.73	72.22	72.19	75.39	69.75	70.23
Al ₂ O ₃	4.60	2.80	3.23	1.97	6.53	4.01	0.44	0.26	8.96	5.51	1.04	0.62
TiO ₂	Trace	...	Trace	...	Trace
Fe ₂ O ₃	0.08	0.03	0.11	0.04	0.13	0.05	0.04	0.01	0.05	0.02
MnO	Trace	...	Trace	...	0.17	0.15	0.21	0.18
CaO	6.76	7.49	7.58	8.31	6.54	7.29	8.36	9.00	0.08	0.09	11.26	12.14
MgO	0.81	1.25	0.25	0.38	Trace	Trace	...
Na ₂ O	15.48	15.53	15.48	15.34	15.92	15.85	18.83	18.34	18.79	19.01	16.54	16.13
K ₂ O	5.56	3.67	2.62	1.71	3.34	2.22	0.66	0.42
SO ₃	0.22	0.16	0.34	0.25
Total	100.17	...	99.89	...	100.09	...	99.72	...	100.02	...	100.07	...
$\Delta E_0/\Delta E_A$, pH 0-10	0.92	...	0.88	...	0.96	...	0.26	...	0.97	...
Conductivity	Very low	...	Good	...	Poor	...	Excellent	...	Good	...	Excellent	...

Table II. Composition of MacInnes-Dole Glasses

Glass	SiO ₂		CaO		MgO		Li ₂ O		Na ₂ O		K ₂ O	
	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %
Potassium	72	77.87	6	6.95	20	19.39	22	15.17
Soda lime	72	72.04	8	8.57	22	21.37
Best soda lime	72	72.17	6	6.44	24	23.36
Soda lime	72	72.33	4	4.30	24	23.34
Soda lime	70	70.21	6	6.45	20	19.39
Soda lime	74	74.17	6	6.44	22	21.40
Soda lime	74	74.30	4	4.30	20	19.39
Lithium	72	58.70	6	5.24	22	36.06
Sodium lithium	72	70.71	6	6.31	2	3.95	20	19.03
Sodium lithium	72	69.29	6	6.18	4	7.74	18	16.78
Potassium lithium	72	66.95	6	5.97	11	20.56	11	6.52
Magnesium	64.5	64.5	10	14.31	25.5	23.73

Table III. Composition of Sskolof and Passynsky Glasses

Glass	SiO ₂		Li ₂ O		Na ₂ O		K ₂ O		CaO		pH Potential in NaOH Solutions
	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %	
Lithium	80	72.18	10	18.17	20	19.39	10	9.65	Linear to pH 12.5
Sodium	72	72.04	8	8.57	Linear to pH 11.0
Potassium	65	70.92	25	17.39	10	11.68	Linear to pH 10.0

Table IV. Composition of Lengyel and Blum Glasses

Glass	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	Potential, Mv. with 0.1 N Sodium	
							pH 6	pH 10
Mole per cent								
Dl	71.5	21	..	8	197	432
Dh	71.5	25	..	3	214	423
Di	71.5	14	..	14	180	420
Dc	64	16	19	181	444
Dv	60	24	..	16	192	422
Dr	58	14	..	14	..	14	-50	-48
Dm	72	14	..	14	-50	-47
Du	61.5	..	11	24	..	3	+30	+27
Da	75	11	3	11	-48	-52
Dg	71.5	28.5	151	314 ^a
Df	76	24	130	350
Dp	67	4	..	22	..	7	201	394
Ds	69	7	..	23	177	313

^a At pH 8.9.

Sskolof and Passynsky (16) studied the behavior of glass electrodes of lithium, sodium, and potassium glass in alkaline solutions containing lithium, sodium, potassium, rubidium, and cesium, using both the Haber and the MacInnes-Dole form of electrodes. They expressed their compositions in weight per cent. In Table III again the equivalent mole per cent has been added. They concluded that the magnitude of the deviations of their electrodes from the standard functions as hydrogen electrodes depends on the radius of the cations situated in the glass as well as in the solution phases. The smaller the radius of the cations in the glass and the larger the radius of the cations in the solution, the smaller were the deviations.

Unfortunately, in subsequent studies in this laboratory a workable glass of the exact lithium oxide-calcium oxide-silica content described by the Russian investigators could not be made. Devitrified and unblowable glasses resulted when this exact composition was attempted. This indicated that more careful study of glass composition and pH response was desirable.

Lengyel and Blum (12) studied the behavior of the glass electrode from the standpoint of chemical composition; they expressed all compositions in mole per cent. In a study of the glasses summarized in Table IV, they observed that their glasses could be classified into two general groups: Dh, Dl, Di, Dc, and Dv glasses, which acted as hydrogen electrodes over the interval of pH 1 to 9; and Dr, Dm, Du, and Da glasses, which acted poorly as hydrogen electrodes but fairly well as sodium electrodes.

Lengyel and Blum used the MacInnes-Dole type of thin glass membrane electrode in all the tests, and concluded that in the sodium oxide-calcium oxide-silica types of glasses, a variation in the amount of the components, or the total substitution of sodium oxide by potassium oxide, caused no change in electrometric behavior. It is unfortunate that their data did not cover the performance at alkalinities in excess of pH 10.0, where the sodium error characteristics may have a greater magnitude. Thus the error of their Ds glass in 1.0 N sodium concentration at pH 10.0 is around 104 mv. (pH 1.7) as compared to their so-called good Dl glass. However, their Dl glass has nearly the same composition as the well-known Corning 015 glass, which has very large sodium errors above pH 10.0. They found that the character of the electrode function was altered when boron trioxide or aluminum oxide was introduced in sodium-calcium types of silicate glasses. Much larger sodium errors were obtained with the last type of glass than with the simple sodium oxide-calcium oxide-silica glasses.

Lengyel and Blum believed that the surface properties of glass are of the greatest importance to the electrometric behavior and are a function of the glass composition, but that the internal structure of a glass is not important.

Dole and Gabbard (2) reported on the properties of lithium glass electrodes. Sskolof and Passynsky's glass, as made by the Corning Glass Works, was produced as an opaque devitrified rod, from which electrodes were made by Dole and Gabbard only after considerable and prolonged heating. The work in this laboratory indicates that such a treatment volatilizes some of the constituents and the resultant glass of the electrode does not have the composition as originally compounded. The glass electrodes used by Dole and Gabbard were of the thin membrane type, probably of uncertain composition. Dole and Gabbard found that the lithium glass electrodes had large and varying asymmetric potentials and failed to function as hydrogen electrodes.

Studies on lithium glasses in this laboratory did not confirm all the conclusions by Dole and Gabbard on lithium glasses. The long continued heating of the lithium oxide-calcium oxide-silica glass rod by Dole and Gabbard might have resulted in an unknown glass composition. This indicated that more data were needed on lithium glasses.

LIMITATIONS OF PRIOR WORK

It is unfortunate that many of the publications upon pH-responsive glasses present the composition data in weight per cent. This may result in misleading comparisons. Comparisons between relative molecules should result in a more logical picture of the problem. This is important when elements of widely different molecular weight are compared.

Many of the early data on the influence of composition upon the pH response were obtained with glass electrodes which had been fabricated in the form of very thin films of glass. The more robust and thicker wall bulb-type of electrode (Haber form) provides better working information, as glass stability may be an important characteristic.

Much of the information has been devoted to soda-lime glasses and only a little to lithia glasses. A wide variety of compositions has not been studied.

MODERN CONCEPTS OF GLASS STRUCTURE

In spite of prior publications, the correct viewpoint as to the mechanism and inner workings of a pH-responsive glass would seem to require a greater knowledge of the constitution of pH glasses.

A systematic study of glass composition was begun in this laboratory more than 8 years ago in an effort to establish the relation of composition to behavior.

An excellent starting point for such a study seemed to be the acceptance of the general picture of glass as presented by B. E. Warren and his associates. X-ray diffraction studies show glass to be amorphous. From a Fourier analysis of the x-ray scattering curves, a fairly good first-order approximation of the picture of soda-silica glasses has been presented (17). In subsequent years potassium-silica glasses, soda lime-silica glasses, lime-phosphate glasses, and lime-borate glasses were studied and the observations fitted into the picture of the general glass structure presented in the earlier paper. Zachariassen (18) has also presented important facts on the vitreous state.

Warren's x-ray studies indicate that in a soda lime-silicate glass neither sodium nor calcium participates in the continuous structure of the silicon-oxygen network. Each silicon is tetrahedrally surrounded by four oxygens at a distance of about 1.62 Å. Part of the oxygens are bounded to 2 silicons and part only to 1 silicon. The sodium and calcium ions are arranged in various holes in the silicon-oxygen network. Each sodium is surrounded by 6 oxygens and each calcium is surrounded by about 7 oxygens. Atomic dimensions therefore become an important factor. This scheme of structure does not repeat identically at regular intervals, and the material is therefore noncrystalline.

Oxygen plays a very important part in silicate glasses. When the alkali and alkaline earth metals are used in glass making they are ultimately introduced as metal oxides by decomposition of carbonates, nitrates, etc. Thus oxygen is present in addition to that added as silica and may take part in the network of the glass structure. The glass structure may be weakened by the change in the geometrical configuration or a change of interatomic forces. Devitrification, chemical disintegration in alkaline solutions, sodium errors, volume electrical conductivity, and similar properties are thus intimately related to the glass structure.

The network former, silicon, and the network-modifying elements, lithium, cesium, barium, strontium, etc., are each bonded to their oxygen neighbors in a different way. The modifier ion may exchange with hydrogen ions in a solution in which a glass is immersed. In this case the silica-oxygen network of the glass may not be destroyed. However, the composition of the glass at the solution interface may be changed by constant exchange of modifier ions. The amount of change should depend upon the nature of the modifier ions within the "holes" of the glass network. Long-time exposures in solutions may be required if the facts are to be established.

The laws of crystal chemistry, the x-ray diffraction study of glass, the various measured physical properties of glass, the kinds of materials, and the ranges of composition in which glass-forming properties exist appear to be involved in an understanding of the mechanism of a pH-responsive glass.

Any explanation of the mechanism of the glass electrode should be consistent with the general scheme of glass structure briefly outlined above. The earlier work on glass composition was not sufficiently broad for application of the more modern concept of structure.

IMPORTANCE OF ION SIZE AND TRACE ELEMENTS

Many different alkali metal-alkaline earth metal-silicate glasses of many possible molecular combinations can be made.

In view of the above suggested nature of glass, it became important in a study of pH-responsive glasses to recognize the ionic radii of the constituent modifiers used in various glasses. Table V indicates the important variation in some radii of the modifying elements of a pH glass (15).

Table V. Crystal Radii of Ions (Pauling)

Element	Valence	Radius, Å.	Ratio of Valence to Radius
Alkali Metals			
Li	1	0.60	1.66
Na	1	0.95	1.06
K	1	1.33	0.75
Rb	1	1.48	0.68
Cs	1	1.69	0.59
Alkaline Earth Metals			
Be	2	0.31	6.45
Mg	2	0.65	3.10
Ca	2	0.99	2.02
Sr	2	1.13	1.77
Ba	2	1.35	1.48

It is equally important to realize that pH-responsive glasses are not definite compounds and may undergo surface changes when the glasses are immersed in aqueous solutions. Base exchange reactions in glasses have been well established.

Early in this work it was recognized that the influence of trace elements may be important. The use of aluminum as a stabilizing element in laboratory glassware has been discussed by Geffcken (5). Thus the presence of 10^{-4} equivalent per liter of aluminum ions in alkaline solutions has been observed greatly to reduce the attack of a laboratory type of glass in alkaline solutions. Whenever an aluminum ion is completely sorbed on the entire glass surface, there is protection from continued action on certain types of laboratory glasses.

Some types of window glass may be attacked by rain water, because the reaction products are continuously removed. At the same time this same glass may show an entirely different sort of attack, if it is immersed in a small volume of water or salt solution where the products of the interaction at the glass interface are not removed.

Tests of pH-responsive glasses immersed in containers of buffer solutions may show a different result than when these same glasses are placed in flow channels in which the surface conditions are constantly changed. In all tests relating composition to pH, the conditions must be carefully specified.

NEED FOR GLASS COMPOSITION DATA

A study of the above information indicated the desirability of producing a complete series of lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, and barium silicate glasses, in order to study the influence of the various metallic ions of varying ionic radii upon the electrical resistance, stability, and pH characteristics of a glass.

Other factors, such as the role of water, must be included in the complete consideration of the mechanism. However, the influence of the glass structure seemed to be fundamental.

The study in this laboratory has involved the preparation of over 500 glasses of different composition. A wide variety of glasses has been prepared in the form of rod. Chemical analyses of these rods indicate that serious changes in chemical composition did not occur between the original mix and the final rod, provided care was taken to produce nondevitrified rod, and to control the temperature of the glass making. Conclusions are questionable except after following the operating performance of a given glass composition in the form of bulbs over a period sometimes in excess of one year. Accordingly, several years have been required to accumulate the fundamental data. These data are rather voluminous and will be presented in a second paper.

SUMMARY

The published information on composition as related to pH characteristics is probably incomplete, owing to the failure accurately to establish the functions of the constituents of a given glass or to employ glass membranes of suitable thickness to assure reproducible results over relatively long periods of time.

Comparisons of pH glass compositions should be made on a mole per cent basis.

It is postulated that the performance of a pH-responsive glass can best be predicted only if the role of the ionic radii of the modifying atoms within the silicon-oxygen glass network is recognized. The stability, base exchange reactions, electrical conductivity, sodium errors, etc., depend upon the ionic properties of the modifier elements as well as on the electrostatic forces prevailing within the interstices of the network.

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Glasses for Measurement of pH

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The data obtained from a study of over 500 different compositions of pH-responsive glasses are summarized and the function of the alkali metals and of the alkaline earth metals is discussed. The nature of the silicon-oxygen (Si-O₄) network is indicated. The pH characteristics of a very large number of glasses are briefly discussed from the viewpoint of molecular composition. The pH-responsive glasses are considered to be structures comprising a silicon-oxygen network in which the alkali metal ions and other metal ions occupy the interstitial positions

within the silicon-oxygen network. The character and dimensions of the ions govern the base exchange reactions and hence the sodium error and stability of the glass. The relative degree of hydration of the lithium ion and its low coordination number with oxygen ions are important considerations for an ideal pH glass. It is not essential that an alkaline earth metal be present in a pH responsive glass. A pH-responsive glass with relatively low sodium error has been made of 28 lithium oxide-3 cesium oxide-4 lanthanum oxide-65 silica.

SOME important publications on the composition of pH glasses have been discussed (6). The modern view of glass composition indicated the need of obtaining controlled data upon the properties of glasses containing alkali (R₂O) metals and alkaline earth (MO) metals of markedly different ionic radii.

It is recognized that on the outer surface of a glass in contact with a solution is developed a potential difference which is independent of the potential developed at the inner glass surface in contact with another solution. It is not easy to discuss a glass with a certain surface composition as independent of the composition of the glass as a whole. The properties of the glass surface are related to the stability of the entire glass aggregate. As a matter of fact, in discussing pH glasses not only must the pH response characteristics be considered, but also the electrical conductivity, durability, and similar properties.

In the production of pH-responsive glass, the first essential is a workable and stable glass. Glasses which easily devitrify, tend towards "seed" formation, have very high softening points, or have insufficient body to draw into rod form or to be blown into bulbs are of little practical utility.

The practical limits in the range of composition of the constituents of pH-responsive silicate glasses are controlled by the resultant electrical resistance of the glass, the softening point, the solubility or stability of the glass, the pH-e.m.f. relationships, and the toughness of the glass.

This study has indicated that many glasses of varying composition can be made which give the theoretical pH-e.m.f. relationships, provided the alkali metal ion content of the test solutions is less than 0.01 N.

This paper merely summarizes the long-duration studies on more than 500 pH-responsive glasses. An effort has been made to present sufficient data to give an adequate picture of what is essential to an understanding of the mechanism of glass electrodes.

LITHIUM GLASSES

When these investigations were initiated over 8 years ago the only available pH-responsive glass was Corning 015, which has

been made available as a result of the work by MacInnes and Dole. This glass had the following mole per cent composition: 21.39% sodium oxide-6.44% calcium oxide-72.17% silica.

Since the inception of this work, the 1190-E and 4990-E blue glass electrodes of the National Technical Laboratories have been made available. No published information on the composition of this glass seems to be available, but it may approach the following mole per cent composition: 25% lithium oxide-8.0% barium oxide-67% silica.

The National Technical Laboratories have made available so-called high temperature glass electrode 1190-T, and it may be assumed that this glass approximates one of the compositions (mole per cent) indicated by Cary and Baxter (3): 19.0% sodium oxide-7.0% calcium oxide-74.0% silica (1); 17.0% sodium oxide-12.5% calcium oxide-70.5% silica (2).

It is understood that the E. D. Coleman Manufacturing Company has produced a lithium type of glass, but no publication has been noted. The Cambridge Instrument Company, in England, is reported to have made lithia-barium-silica types of glasses.

A vast number of trial glasses were made in this laboratory before it was found that a certain favorable silica content, together with additional oxides, was most important if low sodium or potassium errors were to be obtained when such glasses were used for pH-measurements over long periods of time or at elevated temperatures.

It was postulated that the electrical resistance and the sodium error of the various glasses must be due to the nature of the ionic constituents within the silica network. Many data were obtained upon the simple three-component glasses such as lithium oxide-barium oxide-silica. Subsequently tests on more complex systems resulted in radically different types of glasses.

METHODS OF GLASS MAKING

The contradictory literature relative to glass electrode composition and pH behavior indicated that certain variables had not been properly controlled. It was decided to produce each type of glass under controlled temperature conditions and in

platinum crucibles held rigid by the use of an outer ceramic jacket.

Chemically pure carbonates and nitrates of the various metals were used in compounding the glasses and a special glass-maker's sand of low aluminum oxide and ferric oxide content was employed. Glass batches in lots of approximately 113 grams (0.25 pound) each were prepared. A Sentry globar resistor type of electrical furnace was used for the glass production. An automatic temperature control on the furnace was employed and the temperatures were checked by a Leeds & Northrup optical pyrometer. A temperature of 950° C. was used for the initial fusion and this temperature was gradually raised to about 1150° C. The production of the above quantity of glass required very frequent stirring and in general a total time of about 7 to 9 hours at 1150° C. was necessary before complete interaction and uniformity could be obtained. Glass rods were drawn from the melt in the platinum crucible in the form of rods about 6 mm. in diameter and 90 cm. (3 feet) long. These rods were cut to 25-cm. (10-inch) lengths and used for blowing the Haber-type glass electrodes on the ends of glass tubing such as the Corning G-1. This type of lead-glass stem has a very high electrical resistance.

Glass bulbs 9.2 to 9.8 mm. in outside diameter, when made from 0.09 to 0.11 gram of glass, give exceptional reproducibility in electrical resistance, sodium error, solubility, and other characteristics. The wall thickness of such bulbs is surprisingly uniform. The walls are about 0.09 to 0.15 mm. thick.

METHODS OF TESTING

The method of testing the resultant electrodes is of importance.

Six or more electrodes of a given glass were always used for the simultaneous tests. A Leeds & Northrup No. 7655 potentiometer together with a Leeds & Northrup No. 7673 amplifier and a Leeds & Northrup No. 2420b galvanometer were used in the indicating type of measurement of the e.m.f. of the glass-saturated calomel electrodes systems as well as for the hydrogen gas-saturated calomel electrode system. As a matter of fact, the comparisons were actually made between the glass-hydrogen gas electrode system (without liquid junction). The actual pH of the solutions was obtained from the hydrogen gas-saturated calomel electrode system. The temperature of the solutions was read to the nearest

0.1° C. In many tests, particularly at the higher temperatures, the entire solution-electrode system was placed in a controlled-temperature air cabinet in order to assure complete thermal equilibrium for the entire system. Some series of tests were made by immersion of the electrodes in large glass containers in which the buffer solutions were located. Other series of tests have been carried out in flow channels where solution was circulated continuously for 24 hours per day for many weeks. The temperature of such solutions was measured by a Leeds & Northrup resistance thermometer and temperature recorder. The pH values were obtained on a Leeds & Northrup Model S six-point Micromax pH recorder.

One series of glass electrodes was kept in distilled water and removed from time to time in order to check the pH response in solutions of pH 1.0, 6.86, and 12.8 (adjusted to 2 *N* sodium concentration). In the indicating type of tests, a series of pH 1.0, 6.86, 9.18, and 12.8 buffers was used. The exact values of these buffers were obtained by hydrogen gas-saturated calomel electrode measurements. Most of these buffers have been discussed (1, 4, 5). In general, the pH measurements were carried out at intervals of one month over long periods of time, even 4 years.

The limit of error of the direct current electrical resistance measurements was probably on the order of $\pm 10\%$. The limit of error of the pH measurements was on the order of pH ± 0.03 .

STRUCTURE OF GLASS

pH-responsive glasses apparently have the following characteristics:

1. Oxygen ions provide the bulk of the glass network.
2. The network-forming silicon ion holds the oxygen ions together.
3. The network-modifying ions such as lithium, cesium, calcium, strontium, and barium find positions within the "holes" between the network.

It is now generally accepted that when silicon-oxygen (Si-O_4) tetrahedra are held together in such a manner that each oxygen is shared by two tetrahedra an infinite three-dimensional network is present.

The viewpoint was adopted that the nature of a pH-responsive glass depends considerably upon the presence of oxygen ions. Because these oxygen ions are relatively large, they form the greater part of the bulk of a silicate glass. By sharing oxygens the cations tend to hold the negative silicon-oxygen grouping as a unit. These oxygen ions doubtless play an important part in holding other ions rigidly within the network through electrostatic forces.

Biscoe, Druessne, and Warren (2) pointed out, in comparing sodium oxide-silica and potassium oxide-silica types of glasses, that there are two differences which may work in opposite directions. Increasingly large ionic size of the atoms results in a greater distance for the R-O atoms. Thus Warren and his associates found the sodium-oxygen distance to be 2.35 Å., the potassium-oxygen distance to be 2.7 Å., and the silicon-oxygen distance to be 1.62 Å. The force of attraction between the alkali ion within the network and the surrounding oxygens is less for increasing ionic size. However, more oxygen neighbors are bonded to the larger ion than to the smaller ion. The larger ion is held to the structure by progressively weaker bonds, but by more of them than is the smaller ion.

The R-O distance in the glass network is progressively greater as we go from the smaller lithium ion to the larger cesium ion. The force of attraction between the cesium ion and the surrounding oxygens is less than that between the lithium ion and its oxygens. On the other hand, there are more and more oxygen neighbors bonded to the alkali ion as we change from lithium ion progressively to cesium ion in the glass network. The cesium ion is held to the structure by weaker bonds (valence-coordination number) but by many more of the oxygens (larger coordination number) than is the potassium ion or the other smaller diameter ions of the alkali metals. It is not easy to predict whether there will be an increase or a decrease in the tightness with which the

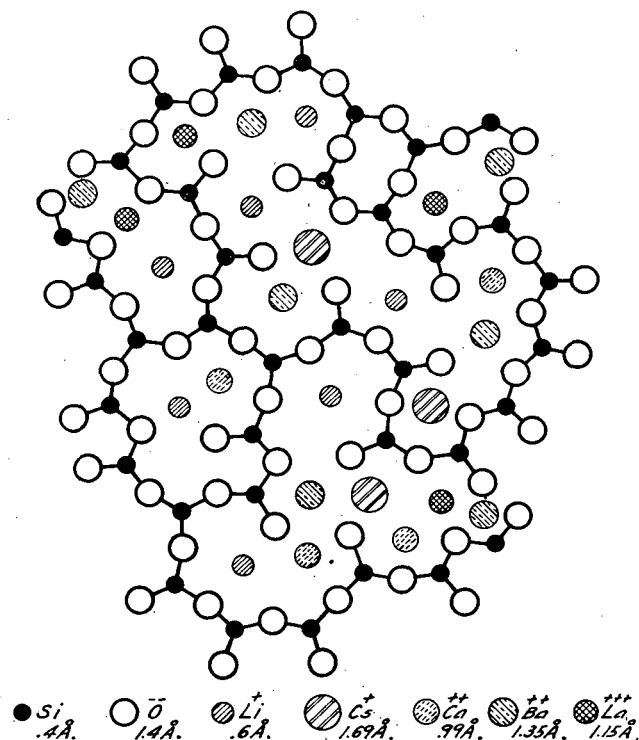


Figure 1. Schematic Representation in Two-Dimensions of Structure of Silica Glass

atom is held within the holes of the silicon-oxygen network when there is change from a lithium oxide type of glass progressively to a cesium oxide type. The data indicate that the larger size cesium or rubidium ions are tightly packed together with their surrounding oxygen ions in the glass network, and as a result are an aid in reducing the tendency towards exchange of sodium ions from the solution into the glass structure.

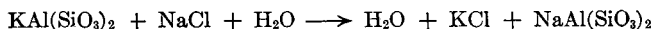
The coordination number (the number of oxygens surrounding a given cation) of the network modifying ions is important in a pH-responsive glass. Potassium ions, with a coordination number of 10, require more oxygens for a given stability than the smaller sodium ions with a coordination number of 6. The x-ray scattering power of the lithium atom is so small compared to oxygen and silicon that few precise data are available on the coordination of the lithium atom. It is indicated in the literature as around 4. This apparently is responsible for one of the several advantages in the use of lithium in pH-responsive glasses. Network-modifying ions with large radii and low valence indicate high coordination number and low bond strength. The stability and sodium ion errors of pH glasses would appear to be correlated in part with the bond strength between the ions which have been selected for a given glass composition.

Some of the zeolites present an interesting comparison to these pH glasses. In the case of the zeolites the interstitial ions can be reversibly replaced without damage to the structure. Even the water which may be present within the interstices may be driven off without damage to the structure. The water may be replaced by alcohols or ammonia.

The great problem in the production of an ideal pH-responsive glass lies in the production of a network structure in which the interchange of hydrogen, sodium, lithium, hydroxyl, etc., ions may be controlled.

Figure 1 may serve to indicate a viewpoint of the general structure of a desirable pH glass.

Thugutt (8) observed that the following reaction took place when leucite was transformed into analcite:



Then too, Vesterberg (9) prepared hydrated lithium metasilicate by treating sodium silicate with lithium chloride or hydroxide. Thus, in general, the above base exchange reactions are an indication of the relative bonding of the respective alkali atoms in certain silicates. This sort of exchange may be involved in a pH-responsive glass.

More facts must be presented before the whole mechanism of the glass electrode can be carefully considered. An attempt has been made to outline in a brief manner the basis of the attack on this problem. Glasses which have alkali metal ions within the silicon-oxygen network may give off cations or exchange them for similar ions. This exchange depends in part upon the size of the ion and the number of oxygen neighbors bonded to the alkali ion and the resultant electrostatic forces prevailing within the glass structure. The ability of the alkali ions to associate with water either as hydration or through purely electrostatic forces is probably an important part of this picture.

Important data have been obtained in the light of the above concept of glass structure. A comparison has been obtained of the influence of relative differences of the alkali metal constituents, of the alkaline earth metal constituents, and of additional oxygen-bearing constituents upon the more important properties of pH glasses.

Table I. Function of R₂O Constituent at 25° C.

(pH response, pH 1 to 7, follows theory)

No.	Composition, Mole Per Cent										Resistance, Megohms	pH Error (2 N Sodium) at pH 12.8, Continuous Use for	
	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O	CaO	BaO	La ₂ O ₃	SiO ₂	1 week		6 months	
431	26	0	0	0	0	0	7	3	64	350	0.10	0.14	
432	0	26	0	0	0	0	7	3	64	200	1.34	1.00	
433	0	0	26	0	0	0	7	3	64	600	2.75	Etched open	
349	25	0	0	0	0	3	5	2	65	750	0.30	0.50	
350	0	25	0	0	0	3	5	2	65	250	1.15	1.25	
351	0	0	25	0	0	3	5	2	65	800	2.43	Etched open	
370	25	0	0	0	0	0	7	3	65	900	0.20	0.20	
382	25	1	0	0	0	0	7	2	65	1600	0.40	0.50	
383	25	0	1	0	0	0	7	2	65	1500	0.30	0.50	
358	25	0	0	0	1	0	7	2	65	1600	0.10	0.20	
328	25	0	0	0	0	3	5	1	66	650	0.35	0.35	
329	25	1	0	0	0	3	5	1	65	1700	0.30	0.35	
330	25	0	1	0	0	3	5	1	65	1000	0.20	0.25	
331	25	0	0	1	0	3	5	1	65	1000	0.12	0.12	
316	25	0	0	0	1	3	5	1	65	500	0.10	0.10	
402	25	0	0	0	0	0	8	0	67	480	0.25	0.60	

Table II. Lithia-Soda Glasses

(Li₂O-Na₂O interchange at 60° C.)

No.	Composition, Mole Per Cent					Resistance, Megohms	pH Error (1 N Sodium) at pH 12.3
	Li ₂ O	Na ₂ O	BaO	La ₂ O ₃	SiO ₂		
431	26	0	7	3	64	19	0.66
473	24	2	7	3	64	155	0.70
478	22	4	7	3	64	760	0.73
470	20	6	7	3	64	4,500	0.8
471	15	11	7	3	64	50,500	1.0
472	10	16	7	3	64	27,500	1.1
479	3	23	7	3	64	140	1.30
432	0	26	7	3	64	7	1.45

FUNCTION OF ALKALI METALS

Table I indicates the influence of the alkaline earth oxide constituents upon the pH response of a glass. The instability of the rubidium and cesium glass-forming compounds, at the temperature of glass making, is such that practical glasses with a high content of either of these two oxides could not be obtained.

Table I, Nos. 431 to 351, indicates the great superiority of a lithium oxide type of glass over the sodium oxide or potassium oxide glasses as related to sodium errors, irrespective of whether it is only a barium oxide or a mixed calcium oxide-barium oxide type of glass. The lower electrical resistance of the sodium oxide types of glasses is also noteworthy. The second part of Table I shows the influence of relatively small amounts of rubidium oxide or cesium oxide as contrasted to sodium oxide or potassium oxide when considering the sodium error.

The pH 1.34 sodium error of the 26 sodium oxide-7 barium oxide-3 lanthanum oxide-64 silica (glass 432 of Table I) in 2 N sodium and pH 12.8 solution appears to be high, yet with the Corning 015 glass consisting of 21.39 sodium oxide-6.44 calcium oxide-72.17 silica the same pH error exists in 2 N sodium at only pH 10.7. Thus glass 432 is greatly superior to Corning 015 glass. The presence of 1 mole % sodium in such a glass as 25 lithium oxide-1 sodium oxide-7 barium oxide-2 lanthanum oxide-65 silica (No. 382 of Table I) results in a sodium error of 0.2 pH greater than in the absence of any sodium in a similar glass when used in a solution of 2 N sodium content and pH 12.8 buffer at 25° C.

Table II indicates the general relationship of the lithium oxide-sodium oxide series of glasses of a alkali metal oxide-barium oxide-lanthanum oxide-silica type.

The data of Table II are very important as far as theory is concerned. It was found impossible to make 25° C. measurements on glasses with compositions between the limits of 22 mole % lithium oxide-4 mole % sodium oxide and 22 mole % sodium oxide-4 mole % lithium oxide because of the very high direct-current electrical resistances of these mixed lithium oxide-sodium oxide types of glasses. Even the measurements at 60° C. were none too easy to carry out. The accuracy of the measure-

ments of the three intermediate glasses, Nos. 470, 471, and 472, is not of the same order as that of the other glasses of this series. However, there is rather good evidence that at 60° C. the sodium error of a glass is definitely related to the mole concentration of sodium in a given glass. The same relative situation would probably be found to exist at 25° C. if sufficiently accurate measurements could be obtained.

Table II indicates that whether a given glass may function purely as a hydrogen electrode or as a sodium electrode is dependent upon the hydrogen ion or sodium ion concentration at the glass-solution interface. If no sodium is present in the glass, or if the glass structure is composed of constituents with bond strengths that prevent base exchange of sodium from the solution, there will be a negligible sodium ion equilibrium at that glass-solution interface. This involves both the specific cations and the oxygens within the glass structure.

A general study of the volumetric direct current electrical resistance of many types of glasses is now being made in an effort to clarify the maxima in the resistance relationships of Table II. However, the 25° C. direct current electrical resistance of millions of megohms for such a glass as the No. 471 of 15 lithium oxide-11 sodium oxide-7 barium oxide-3 lanthanum oxide-64 silica involves great experimental difficulties in the measurement of pH.

It is postulated that the atoms of the silicon-oxygen network are oscillating about some mean position. Under the influence of an electric field the loosely held lithium ions can migrate, or jump, from one "hole" of the network to an adjacent hole. In the absence of any applied electric field the lithium ions may migrate equally in all directions. However, under the influence of an electrical field the lithium ions will tend to move in the

direction of the field. For the process of electrical conductivity it would be expected that, in general, the larger the alkali ion the slower the migration of that ion through the holes of the silicon-oxygen network. Divalent alkaline earth ions have stronger electric fields than the monovalent alkali ions. A calcium ion has about the same size as a sodium ion, but it should give a much smaller electrical conductivity because it is a divalent ion and therefore bonded more tightly to the surrounding oxygens of the glass network. When jumping to another hole, or interstice, the lithium ion has to go from one energy level to a second energy level. The number of jumps per unit time depends on the frequency of vibration of the ion, the temperature, and the nature of the silicon-oxygen network.

There is a possibility that the much larger hydration of the lithium ion over the sodium, potassium, cesium ion may play an important role in the relative electrical conductivities of these glasses. The higher electrical resistance of the lithium oxide glasses over the sodium oxide glasses of similar composition of Table I may be related to the relative hydration of the lithium ions in the interstitial positions of the glass network.

The lithium oxide content of glasses greatly influences the direct current electrical resistance of a pH-responsive glass. Table III indicates the general trend when the lithium oxide content is simultaneously changed with lanthanum oxide. In most cases 25 mole % lithium oxide results in a more stable and robust glass than a 28 mole %. The sodium error of a 24 mole % lithium oxide glass is considerably less than that of a 28 mole % lithium oxide glass. The working qualities of a glass having much over 28 mole % lithium oxide were inferior, owing to devitrification. Glasses of high lithium oxide content with simultaneously relatively low silica content are not practical to manufacture. The solubility of a 28 mole % lithium oxide glass is much greater at 90° C. than a 25 mole % lithium oxide glass of similar composition as regards the other constituents.

Table III. Lithium Oxide Influence at 25° C.

(pH response, pH 1 to 7, follows theory).

No.	Composition, Mole Per Cent						Resistance, Megohms	pH Error (2 N Sodium) at pH 12.8 after 1 Month of Use
	Li ₂ O	Cs ₂ O	CaO	BaO	La ₂ O ₃	SiO ₂		
5-Component Glasses								
389	25	2	0	4	6	63	700	0.08
463	26	2	0	4	5	63	400	0.10
464	27	2	0	4	4	63	270	0.10
465	28	2	0	4	3	63	70	0.12
6-Component Glasses								
364	24	2	4	4	3	63	5200	0.08
379	25	2	2	5	3	63	1500	0.10
365	26	2	4	4	1	63	1300	0.10
440	27	2	3	2	3	63	270	0.15
456	28	2	3	2	2	63	110	0.20

FUNCTION OF ALKALINE EARTH METALS

Table IV presents the facts relative to the alkaline earth metal constituents of a pH-responsive glass. The influence of ionic size of the divalent elements on the direct current electrical resistance and on the glass stability in alkaline solutions is clearly indicated. The superiority of the barium oxide and strontium oxide types of glass over the calcium oxide, magnesium oxide, or beryllium oxide types is of considerable importance. The use of the larger size alkaline earth ions in the interstitial positions of the glass network has a very definite blocking action on base-exchange reactions as indicated in the author's patent (7).

This is most important when considering glasses of low sodium error.

In general, a 25 lithium oxide-1 to 2 cesium oxide-7 to 8 alkaline earth oxide-1 to 3 lanthanum oxide-63 to 65 silica type of glass is most stable, gives the lowest sodium error, but has the highest direct current electrical resistance when the alkaline earth constituents are either strontium oxide or barium oxide. A decreased electrical resistance can be obtained by using a calcium oxide-strontium oxide or a calcium oxide-barium oxide combination in the above glass without serious sacrifice in sodium

Table IV. Function of Alkaline Earths at 25° C.

No.	Composition, Mole Per Cent										Original Resistance, Megohms	Equivalent pH Error (2 N Sodium), at pH 12.8, after Continuous Use for			
	Li ₂ O	Cs ₂ O	BeO	MgO	CaO	SrO	BaO	La ₂ O ₃	SiO ₂	After 1 year		1 week	6 months	1 year	
359	25	0	7	0	0	0	0	3	65	100	195	2.5	2.5	2.5	
367	25	0	0	7	0	0	0	3	65	140	250	1.1	1.1	1.1	
368	25	0	0	0	7	0	0	3	65	500	712	0.5	0.5	0.6	
369	25	0	0	0	0	7	0	3	65	900	1050	0.3	0.4	0.5	
370	25	0	0	0	0	0	7	3	65	900	960	0.2	0.2	0.35	
354	25	1	7	0	0	0	0	2	65	140	380	1.9	1.9	1.9	
355	25	1	0	7	0	0	0	2	65	900	825	0.9	0.9	0.9	
356	25	1	0	0	7	0	0	2	65	1200	1100	0.4	0.4	0.5	
357	25	1	0	0	0	7	0	2	65	1600	1250	0.15	0.2	0.3	
358	25	1	0	0	0	0	7	2	65	1600	1200	0.1	0.15	0.25	
314	25	1	3	0	0	0	5	1	65	300	620	0.35	0.40	0.50	
315	25	1	0	3	0	0	5	1	65	750	1040	0.25	0.25	0.50	
316	25	1	0	0	3	0	5	1	65	500	725	0.10	0.10	0.15	
322	25	1	5	0	3	0	0	2	64	300	635	0.75	0.80	0.90	
323	25	1	0	5	3	0	0	2	64	850	1500	0.50	0.50	0.70	
325	25	1	0	0	3	5	0	1	65	600	1000	0.20	0.20	0.25	
379	25	2	0	0	2	0	5	3	63	1500	1260	0.10	0.10	0.10	
469	25	2	0	0	0	3	5	2	63	600	600	0.10	0.08	0.10	
401	25	2	0	0	2	5	0	2	64	1300	800	0.10	0.12	0.20	

Table V. Barium Oxide and Calcium Oxide Influence at 25° C.

(pH response, pH 1 to 7, follows theory)

No.	Composition, Mole Per Cent						Resistance, Megohms	pH Error (2 N Sodium) at pH 12.8 after 3 Months of Use
	Li ₂ O	Cs ₂ O	CaO	BaO	La ₂ O ₃	SiO ₂		
400	25	2	8	0	2	63	1000	0.10
398	25	2	6	2	2	63	1200	0.10
397	25	2	4	4	2	63	1350	0.10
396	25	2	2	6	2	63	1500	0.10
388	25	2	0	8	2	63	1700	0.08

error. This feature may be of considerable importance when pH measurements have to be made at relatively low temperatures.

From the standpoint of direct current electrical resistance a properly proportioned lithium oxide–beryllium oxide–silica type of glass provides a most interesting relatively high electrical conducting medium. A number of lithium oxide–beryllium oxide–silica glasses have been studied. Certain compositions show very little pH response in the alkaline range.

The influence of varying ratios of calcium oxide and barium oxide in a glass is worthy of consideration, particularly from the viewpoint of the direct current electrical resistance of similar glass membranes. Table V indicates the general relationships for glasses of the type containing 25 lithium oxide–2 cesium oxide–8 alkaline earth oxide–2 lanthanum oxide–63 silica. Just as long as there are 2 mole % lanthanum oxide and 63 mole % silica in a glass, whether there is barium oxide or calcium oxide has little influence on the sodium error at 25° C. It is obvious that the larger barium ion has a pronounced influence on the electrical resistance of a given glass. This behavior confirms the general idea expressed above in the consideration of electrical conductivity. The interchange of barium oxide and calcium oxide for glasses of 70 silica content is not so favorable for sodium errors as with the 2 lanthanum oxide–63 silica types of glass.

SILICON-OXYGEN NETWORK

The information thus far presented indicates the great superiority of certain compositions as far as sodium error is concerned. A silicate–strontium oxide or barium oxide type of glass containing lithium oxide and small amounts of rubidium oxide or cesium oxide has distinct advantages. However, the alkali and alkaline earth constituents are not the only essential consideration. For long-time operation or at elevated temperatures, the actual silicon-oxygen (Si-O₄) network structure, together with oxygen-containing constituents, governs the glass stability. A lithium oxide type of glass having an adequate number of unsaturated single-bonded oxygens appears to be relatively easy to produce. This type of glass offers distinct advantages.

Table VI indicates the importance of the control of the silica-oxygen constituents of even a simple lithium oxide–barium oxide glass. Thus in this type of glass a 67 mole % silica has a smaller sodium error than a 63 mole % silica. The influence of oxygen in the network appears to be important. However, none of these simple three-component

glasses shows the desirable stability at either 25° C. over long periods of time or at temperatures of 70° to 80° C.

The data of Table VI show the importance of a relatively low silicon content if associated with an auxiliary adequate oxide source. The relative performance of glasses 402 (25 lithium oxide–8 barium oxide–67 silica) and 388 (25 lithium oxide–2 cesium oxide–8 barium oxide–2 lanthanum oxide–63 silica), as far as sodium error and stability are concerned, is most important. Even for such a high lithium oxide content as 28 mole % in glass 399 it is interesting to note the stabilizing influence of the 63 silica–2 lanthanum oxide composition as contrasted to glass 402 which has the more favorable 25 mole % lithium oxide, but a 67 mole % silica and no lanthanum oxide. Again, the great superiority of glass 411 with 2 mole % lanthanum oxide and 64 mole % silica over No. 362 with no lanthanum oxide and 64 mole % silica, is most interesting.

It would appear better to provide a desirable high oxygen content by the use of certain desirable oxides than by means of increased silica content.

It was found impossible to produce homogeneous nondevitrifying glasses with lithium oxide–barium oxide–lanthanum oxide having less than 59 mole % silica.

The stability of the glasses at temperatures over 25° C. is of great interest. Table VII indicates the importance of the silica-oxygen composition as related to 90° to 95° C. operation. Glass electrodes were operated continuously in flowing city water at 90° to 95° C. They were removed each week from the flow channels and checked at 50° C. in a pH 12.2 buffer having a 2 N sodium content.

Tests in hot flowing municipal water present a more severe treatment for a pH glass than those in which many salt solutions are employed. As a matter of fact, every test condition represents a specific treatment of the glass. With continuous flow of the solutions past an electrode, city water gives a certain useful life, 1 N sodium salt at pH 7.0 gives another result, and 1 N sodium salt at pH 10.0 gives still a different result. Any statement relative to stability of a given glass electrode must be

Table VI. Silicon Oxide–Lanthanum Oxide Behavior at 25° C.

(pH response, pH 1 to 7, follows theory)

No.	Composition, Mole Per Cent						Resistance, Megohms	Continuous Use, pH Error (2 N Sodium) at pH 12.8	
	Li ₂ O	Cs ₂ O	CaO	BaO	La ₂ O ₃	SiO ₂		For 1-week	For 4 months
402	25	0	0	8	0	67	480	0.25	0.60
376	25	1	0	9	0	65	700	0.60	1.80
387	25	2	0	10	0	63	750	1.50	2.80
388	25	2	0	8	2	63	1700	0.06	0.08
358	25	1	0	7	2	65	1600	0.10	0.20
377	25	1	0	4	5	65	700	0.13	0.20
361	25	0	0	5	4	66	450	0.30	0.35
362	26	2	3	5	0	64	750	0.10	3.00
365	26	2	4	4	1	63	1300	0.10	0.08
399	28	2	0	5	2	63	100	0.06	0.07
360	28	2	2	3	0	65	85	0.70	2.00
429	26	1	2	3	1	67	200	0.27	0.40
410	25	2	2	4	1	66	450	0.20	0.20
426	26	2	4	2	2	64	500	0.10	0.10
411	26	2	2	4	2	64	450	0.10	0.08
379	25	2	2	5	3	63	1500	0.10	0.10
390	27	1	2	2	1	67	70	0.40	0.70
407	27	2	2	2	1	66	105	0.25	0.65
403	27	2	2	2	2	65	115	0.20	0.30
404	27	2	2	2	4	63	220	0.15	0.10

Table VII. Glass Stability in City Water at 90° to 95° C.

No.	Composition, Mole Per Cent						pH Error at 50° C. in 2 N Sodium, pH 12.2			
	Li ₂ O	Cs ₂ O	CaO	BaO	La ₂ O ₃	SiO ₂	Start	After 1 week	After 6 weeks	After 12 weeks
402	25	0	0	8	0	67	0.86	2.00		
287	24	2	3	3	0	68	0.40	1.60	2.20	..
289	25	1	3	4	0	67	0.50	1.10	1.65	..
327	25	2	2	3	1	67	0.45	1.40	1.70	..
364	24	2	4	4	3	63	0.25	0.05	0.08	0.08
371	24	2	2	4	5	63	0.25	0.12	0.08	0.09
365	26	2	4	4	1	63	0.30	0.30	0.35	0.32
373	25	2	2	4	4	63	0.25	0.11	0.08	0.15
379	25	2	2	5	3	63	0.30	0.12	0.08	0.15
388	25	2	0	8	2	63	0.25	0.16	0.10	0.25

Table VIII. Effect of Oxygen Modifiers at 25° C.

(Composition, mole per cent. 26 Li₂O-2 Cs₂O-2 CaO-4 BaO-2 modifier-64 SiO₂)

No.	Modifier	Resistance, Megohms		pH Error (2 N Sodium) at pH 12.8 after Continuous Use for		
		After 2 days	After 1 year	2 days	6 months	1 year
411	La ₂ O ₃	450	550	0.07	0.07	0.10
415	CeO ₂	480	520	0.10	0.12	0.12
413	Pr ₂ O ₃	450	530	0.07	0.10	0.20
414	Nd ₂ O ₃	450	475	0.08	0.15	0.20
455	TeO ₂	380	500	0.17	0.20	0.23
423	P ₂ O ₅	150	235	0.32	0.20	0.25
417	TiO ₂	280	430	0.10	0.25	0.25
458	MnO ₂	480	500	0.20	0.26	0.80
457	Mn ₂ O ₃	1300	1800	0.20	0.24	0.30
430	CoO	420	557	0.25	0.30	0.38
418	ZrO ₂	250	360	0.20	0.33	0.57
452	Cb ₂ O ₅	210	330	0.16	0.35	0.49
421	Ta ₂ O ₅	200	355	0.12	0.40	0.45
420	ThO ₂	280	370	0.12	0.40	0.47
412	Co ₂ O ₃	2400	2800	0.30	0.30	0.92
425	As ₂ O ₃	190	325	0.40	0.46	1.06
419	UO ₂	300	435	0.25	0.47	1.50
424	B ₂ O ₃	360	485	0.22	0.50	0.66
444	Cr ₂ O ₃	200	366	0.17	0.50	1.03
427	WO ₃	380	425	0.17	0.54	1.20
454	SeO ₂	200	302	0.25	0.90	0.90
416	Al ₂ O ₃	290	470	0.25	1.10	0.82
422	V ₂ O ₅	200	310	0.58	1.06	0.85
428	MoO ₃	150	350	0.31	1.10	1.85
453	Tl ₂ O ₃	720	880	0.60	2.90	3.26

qualified by presenting the exact conditions of use. In general, the smaller the salt concentration and the higher the pH of a solution, the less stable is a given glass electrode.

Table VII indicates the great superiority of a 63 mole % silica glass with an adequate oxygen modifier over a 67 mole % silica glass without an oxygen modifier. These and other tests at temperatures of 75° to 80° C. in 1 N sodium concentration and pH 10.0 have indicated that a glass with 4 mole % of lanthanum oxide, or higher, shows a glass surface etching which is not present in the 1, 2, or 3 mole % lanthanum oxide content. Hence, there are well defined limits for the concentration of the oxygen modifiers. The data indicate that 2 mole % of lanthanum oxide is the most desirable.

OXYGEN MODIFIERS

The use of lanthanum oxide in the composition of these glasses introduced the question as to the function of such a constituent. The function of lanthanum oxide might be that of a specific stabilizing by the lanthanum ions similar to that of the aluminum ions in glassware in order to reduce the attack in alkaline solu-

tions. The influence could in part be due to the introduction of a desirable content of single-bonded oxygen atoms within the glass network.

Very small amounts of certain constituents have a pronounced influence on the properties of a glass. When a small amount of aluminum oxide is added to silica the aluminum tends to go into tetrahedral coordination. The aluminum ion being trivalent, the four oxygens bonded to an aluminum ion are unsaturated. Those regions where the unbalanced negative charge exists tend to show an attraction for positively charged ions which may be present within the "holes" of the glass network. This then exerts a stabilizing influence upon the glass. The addition of boron trioxide to silica does not result in unsaturated oxygens, so no stabilizing influence is observed.

It seemed probable that the rare earth oxides, which in general are trivalent and not easily attacked by alkali, might offer great promise as stabilizers in a pH glass network. Information on a wide variety of oxygen modifiers seemed desirable.

In order to study the influence of "oxygen modifiers" a series of glasses was made with the following mole per cent compositions: 26 lithium oxide-2 cesium oxide-2 calcium oxide-4 barium oxide-2 modifier-64 silica.

The data on these glasses are presented in Table VIII. It appears that the rare earth oxides exert a greater stabilizing influence than most other oxides. However, the behavior of phosphorus pentoxide, tellurium trioxide, and titanium dioxide are also favorable. In general, the oxides most easily attacked by sodium hydroxide solutions are the poorest stabilizers. The advantage of lanthanum oxide over aluminum oxide is most interesting.

It is also important to contrast the long-time stability of many of the glasses of Table VIII to glass 362 (Table VI), which with a mole composition of 26 lithium oxide-2 cesium oxide-3 calcium oxide-5 barium oxide-0 lanthanum oxide-64 silica corresponds closely to those of Table VIII except that it contains no lanthanum or other oxygen modifier. This particular glass has exceedingly poor stability as contrasted to most of the glasses of Table VIII.

SIMPLE ALKALI METAL SILICATE GLASSES

It had been assumed that pH-responsive glass must be made from a combination of an alkali metal and an alkaline earth metal with silica. The data thus far presented indicate that the alkaline earth metal with the largest ionic radius has advantages

as far as sodium error is concerned, when an alkaline earth metal is used in combination with lithium oxide, cesium oxide, lanthanum oxide, and silica.

In an effort to establish the true mechanism of the pH-responsive characteristics of a glass it seemed desirable to learn just what constituents of a glass were responsible for the pH response. All the data indicated that at least a highly hydrated alkali metal ion was desirable. The superiority of the lithium oxide, rubidium oxide, or cesium oxide constituents of a silica glass has been indicated. It seemed desirable to observe the behavior of glasses that contained no alkaline earth metal constituent.

Table IX. Glasses without Alkaline Earth Metal Constituents at 25° C.

No.	Composition, Mole Per Cent							Resistance, Megohms	pH Response, pH 1 to 9	pH Error in 2 N Sodium, pH 12.8, after Continuous Use for		
	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O	La ₂ O ₃	SiO ₂			5 days	1 month	6 months
487	30	0	0	0	2	2	66	-15	Follows theory	0.60	1.03	1.50
491	28	0	0	0	3	4	65	35	Follows theory	0.15	0.10	0.20
490	27	0	0	0	3	3	67	38	Follows theory	0.25	0.35	0.40
494	28	0	0	0	3	5	64	38	Follows theory	0.19	0.08	0.09
498	28	0	0	3	0	5	64	86	Follows theory	0.30	0.24	0.70
505	28	0	0	3	0	4	65	71	Follows theory	1.30	0.35	0.70
501	28	0	3	0	0	5	64	77	Follows theory	1.00	1.15	1.20
508	28	0	3	0	0	4	65	60	Follows theory	1.30	1.50	1.66
500	28	3	0	0	0	5	64	281	Follows theory	1.21	1.55	1.55
507	28	3	0	0	0	4	65	220	Follows theory	1.60	1.72	2.00
502	28	0	0	3	2	4	63	103	Follows theory	0.35	0.30	0.60
509	26	0	0	3	2	4	65	190	Follows theory	0.10	0.20	0.80
499	26	2	0	0	3	5	64	2091	Follows theory	0.15	0.10	0.05
506	26	2	0	0	3	4	65	900	Follows theory	0.12	0.11	0.25
514	26	0	3	0	2	4	65	46	Follows theory	0.35	0.34	0.80
496	28	0	0	0	0	5	67	26	Follows theory	1.30	1.35	1.35
486	28	0	0	0	2	2	68	40	Follows theory	0.70	0.85	1.13
515	28	0	0	0	3	4 Pr ₂ O ₃	65	32	Follows theory	0.17	0.28	0.40
516	28	0	0	0	3	4 TiO ₂	65	5	Follows theory	1.20	2.00	2.80
503	28	0	0	0	3	4 MnO ₂	65	112	Follows theory	1.66	1.80	2.90
504	28	0	0	0	3	5 Mn ₂ O ₃	64	6613	Follows theory	0.30	0.20	0.50
495	28	0	0	0	3	0 La ₂ O ₃	69	10	-pH 0.10 error	1.85	2.50	2.50
488	0	28	0	0	2	2 La ₂ O ₃	68	5	-pH 0.50 error	2.70	Glass dissolved	
489	0	0	28	0	2	2 La ₂ O ₃	68		Too high melting to blow bulbs			

Table IX summarizes the behavior of glasses which consist of lithium oxide, cesium oxide, lanthanum oxide, and silica.

The simple type of glasses which contain a relatively high lithium oxide content show exceptionally low resistances. The sodium error of glass 491 of Table IX consisting of 28 lithium oxide-3 cesium oxide-4 lanthanum oxide-65 silica, or of glass 494 consisting of 28 lithium oxide-3 cesium oxide-5 lanthanum oxide-64 silica, is not greatly different from that of glass 475 of Table III consisting of 28 lithium oxide-2 cesium oxide-4 barium oxide-3 lanthanum oxide-63 silica.

The low resistance of glass 488 of Table IX, consisting of 28 sodium oxide-2 cesium oxide-2 lanthanum oxide-68 silica, is consistent with the relative behavior of those glasses of Table I. As a pH-responsive glass this sodium oxide glass is not as inviting as those sodium oxide glasses containing alkaline earth metal oxides, such as glass 432 of Table I. The solubility of this glass makes it impractical to use. This is in great contrast to the more stable lithium oxide types of glass.

The influence of the cesium oxide content of these glasses is indicated by comparison of glass 496 of Table IX consisting of 28 lithium oxide-5 lanthanum oxide-67 silica, having a 25° C. sodium error of pH 1.30 in a pH 12.85 solution of 2 *N* sodium concentration, to glass 494 of 28 lithium oxide-3 cesium oxide-5 lanthanum oxide-64 silica, with a sodium error of only pH 0.25. The lower silica content of glass 494 is not wholly responsible for the greatly reduced sodium error of that glass. Thus the influence of cesium oxide in the nonalkaline earth metal oxide type of glasses is similar to that in glasses containing alkaline earth metal oxides.

The role of cesium oxide in these simple glasses is perhaps best indicated in glasses 491, 507, and 508 of Table IX. The following specific comparisons from that table are of considerable interest.

Glass No.	Composition, Mole Per Cent	Sodium Error, pH 12.8, 2 <i>N</i> Na		25° C. Resistance, Megohms		Resistance, Increase Factor
		Original pH	After 1 year pH	Original	After 1 year	
491	28 Li ₂ O-3 Cs ₂ O-4 La ₂ O ₃ -65 SiO ₂	0.15	0.27	35	133	3.8
508	28 Li ₂ O-3 K ₂ O-4 La ₂ O ₃ -65 SiO ₂	1.30	1.96	60	163	2.7
507	28 Li ₂ O-3 Na ₂ O-4 La ₂ O ₃ -65 SiO ₂	1.60	2.00	220	378	1.7

The relative influence of addition of cesium oxide to lithium oxide as contrasted to potassium oxide and sodium oxide on the resultant sodium error is most worthy of note. The addition of cesium oxide, potassium oxide, or sodium oxide to a lithium oxide-lanthanum oxide-silica glass as related to the magnitude of the electrical resistance is of considerable importance.

If stability of a pH glass is measured in part by the constancy of its electrical resistance over long periods of use, the above data indicate that the lithium oxide-sodium oxide types of glasses are the most stable.

The role of the silica-lanthanum oxide ratio is indicated by a comparison of glass 495 of Table IX consisting of 28 lithium oxide-3 cesium oxide-0 lanthanum oxide-69 silica having a 25° C. sodium error of pH 1.85 in a pH 12.85 solution of 2 *N* sodium concentration to glass 491 consisting of 28 lithium oxide-3 cesium oxide-4 lanthanum oxide-65 silica having a sodium error of only pH 0.15 under similar conditions.

The most noteworthy contrast in the nonalkaline earth metal oxide types of glasses to those containing these metal oxides is the influence of the oxygen modifiers. The rare earth oxides, such as lanthanum oxide or praseodymium oxide, are effective stabilizers in either type of glass. However, titanium dioxide and manganese dioxide have a much greater stabilizing influence on the alkaline earth metal oxide type of glasses, as indicated in Table VIII, than in the simpler types of glasses of Table IX.

In other characteristics the simple type of lithium oxide-cesium oxide-lanthanum oxide-silica glasses have a close similarity to similar glasses containing calcium oxide or barium oxide.

The coefficient of expansion and the melting point of the glass 489 of Table IX, consisting of 28 potassium oxide-2 cesium oxide-2 lanthanum oxide-68 silica, were such that it could not be sealed to available high electrical resistant stem glasses such as the Kimble N51A, Corning G-1, or Pyrex glasses. At least, this particular composition of glass is not inviting from a practical production point of view.

The lithium oxide type of glasses of Table IX were tested in continuously circulated solutions of pH 11.0 containing a 1 *N* sodium content and at 90° C. for over 2 months. Such glasses as Nos. 490 and 491 were found surprisingly stable even in the pH 11.0 range at these high temperatures.

It seemed desirable to produce a series of glasses of the alkaline earth metal oxide-lanthanum oxide-silica type corresponding to the alkali metal glasses of Table IX. It was not possible to fuse these particular glasses of 28 mole % calcium oxide, or of 28 mole % beryllium oxide, even at a temperature of 1600° C. Producing these glasses in platinum dishes and sealing them to high electrical resistant glass stems were not practical.

The data on the glasses of Table IX offer much as a simple starting point in the analysis of what may be responsible for the pH response of a glass. They indicate that the alkali metal constituent of a glass is closely related to the pH response characteristics of the glass. In fact, this would appear the essential constituent for pH response. All these alkali metals are characterized by solvation of water, or its equivalent, with their ions at least in aqueous solutions.

The third paper in this series will discuss the mechanism of the glass electrode in light of the data presented in this paper.

ELECTRICAL RESISTANCE OF GLASSES

This subject is being treated in a separate paper. However, a study of the stability of the electrical resistance of glass electrodes which have been continuously used in aqueous solutions at 25° C. for one year has brought out some important features.

Typical data, summarized in Table X, indicate that the maximum stability of electrical resistance can be obtained in lithia-silica types of glasses only if the lithium oxide content is below 25 mole % and if the silica content is relatively low, or below 63 mole %. There is also distinct advantage in the use of a barium oxide or a strontium oxide type of lithia glass over a calcium oxide, magnesium oxide, or beryllium oxide type of lithia-silica glass.

The data indicate, if the continued constancy of electrical resistance of a lithia type of pH glass is to be obtained, that such a glass must have a relatively high initial resistance at 25° C.

High lithium oxide content of pH glasses, which favor initially low electrical resistance, is always associated with relatively large increases in resistance with time of use. Thus, it is not easy to produce robust types of glass electrodes which have relatively low and stable electrical resistances.

The soda types of pH-responsive glasses show less resistance aging characteristics than the lithia types of glasses of equivalent composition.

SUMMARY

Complex pH-responsive glasses consisting of suitable mole percentages of lithium oxide-cesium oxide-barium oxide-lanthanum oxide-silica, or lithium oxide-cesium oxide-calcium oxide-barium oxide-lanthanum oxide-silica, give relatively low sodium errors and good stability at temperatures up to 95° C. Strontium oxide may replace barium oxide in the above glasses with a negligible change in the characteristics. A mixed calcium oxide-barium oxide or calcium oxide-strontium oxide offers certain advantages in electrical resistance and low sodium error.

The sodium error of a pH-responsive glass is related to the ionic radius of the constituent alkali metal ions and alkaline earth metal ions within the silicon-oxygen network. A lithium oxide-

Table X. Composition-Electrical Resistance of pH Glasses at 25° C.

(Glass bulbs 9- to 10-mm. O.D., 0.1 gram of glass per bulb)

No.	Composition, Mole Per Cent								Resistance		Resistance Increase Factor
	Li ₂ O	Cs ₂ O	BeO	MgO	CaO	BaO	La ₂ O ₃	SiO ₂	Original	After 1 year	
359	25	0	7	0	0	0	3	65	100	198	2.0
367	25	0	0	7	0	0	3	65	140	250	1.8
368	25	0	0	0	7	0	3	65	500	712	1.4
370	25	0	0	0	0	7	3	65	900	960	1.1
364	24	2	0	0	4	4	3	63	5200	5200	1.0
379	25	2	0	0	2	5	3	63	1500	1500	1.0
365	26	2	0	0	4	4	1	63	1300	1600	1.0
441	27	2	0	0	3	2	3	63	265	390	1.5
456	28	2	0	0	3	2	2	63	110	344	3.1
429	26	1	0	0	2	3	1	67	200	300	1.5
426	26	2	0	0	4	2	2	64	500	640	1.3
411	26	2	0	0	2	4	2	64	450	550	1.2
365	26	2	0	0	4	4	1	63	1300	1600	1.2

cesium oxide type of glass favors low sodium errors. A strontium oxide or barium oxide constituent also favors low sodium errors. A relatively low silica content in combination with the correct modifying oxide is favorable for low sodium errors and the highest stability of pH glasses.

The direct current electrical resistance of a pH-responsive glass is related to the radius of the ionic constituents of a glass. A 28 mole % lithium oxide content, an alkaline earth metal of small ionic radius, and a 70 mole % silica content favor a relatively low direct current electrical resistance. In general, a composition giving a low electrical resistance type of glass will give relatively high sodium errors. Soda types of glasses result in lower electrical resistance than the equivalent lithia types of glasses.

The use of 60 to 63 mole % of silica in combination with from 1 to 3 mole % of lanthanum oxide, or rare earth oxide, and lithium oxide and cesium oxide, results in very favorable pH-responsive glasses with relatively low sodium errors.

It is not essential that an alkaline earth metal be present in a pH-responsive glass. A pH-responsive glass with relatively low

sodium error has been made of 28 lithium oxide-3 cesium oxide-4 lanthanum oxide-65 silica.

The pH characteristics of a very large number of glasses have been briefly discussed from the viewpoint of molecular composition. The pH-responsive glasses have been considered to be structures comprising a silicon-oxygen network in which the alkali metal ions and other metal ions occupy the interstitial positions within the silicon-oxygen network. The character and dimensions of the ions govern the base exchange reactions and hence the sodium error and stability of the glass. The relative degree of hydration of the lithium ion and its low coordination number with oxygen ions are important considerations for an ideal pH glass.

The composition of the most practical pH-responsive glass represents a compromise in which greatest stability with minimum sodium error and relatively low direct current electrical resistance are obtained.

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DIFFERENTIAL THERMOMETER

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Differential thermometers filled with liquids other than water have been constructed and tested. Although no radical increase in thermometer sensitivity can be achieved by their use, it is possible to secure maximum sensitivity for a wide range of ebulliometric solvents by the proper choice of thermometer liquid. These thermometers have been used in semiroutine analyses for some time with satisfactory results.

THE theory of the differential thermometer was first outlined by Menzies (6) in 1920. Together with Wright (7) he demonstrated its value in ebulliometric molecular weight determinations. Although several workers have reported using the thermometer (3, 4, 8), none has published any attempt to improve the thermometer's range or sensitivity.

The ebulliometric method of Menzies and Wright (7) has been used, with slight modifications, for molecular weight determinations in this laboratory for a number of years. The method was severely circumscribed, however, because of the limitations of the water-filled thermometer. The sensitivity of the thermometer, in ° C. per mm., drops off rapidly below the boiling point of water, thereby greatly limiting the number of organic solvents with which it could be used. Furthermore, according to the procedures of the above noted investigators, the thermometer was not used

much above the boiling point of water. Menzies (6) pointed out these difficulties and an obvious solution, which was to fill the thermometer with a liquid other than water.

The present research was undertaken to prepare thermometers filled with liquids other than water and to devise, if possible, a more sensitive differential thermometer. Since its completion, Barr and Anhorn (2) have described another method of filling thermometers with nonaqueous liquids.

APPARATUS AND CHEMICALS

A standard high vacuum bench, capable of reaching vacuums better than 10^{-5} mm. of mercury, was used in much of the filling work. Liquid nitrogen, dry ice-methanol, and water ice-methanol were used as refrigerants for handling liquids used in filling the thermometers. A small tube furnace, 2.5 cm. (1 inch) in diameter \times 30 cm. (12 inches) long, was used for outgassing the

thermometer bodies. The current to the heater was adjusted to give a temperature of 530° C.

Thermometer bodies were constructed of No. 774 Pyrex brand glass tubing of suitable size. No special effort was made to secure tubing of uniform bore.

Pure liquids for filling the thermometers were secured by a variety of methods. All except the *p*-xylene and sulfur dioxide were distilled at least once from the best obtainable grades. The former was Standard Sample 215-5 from the National Bureau of Standards and was used without further purification. The latter was taken directly from a cylinder of refrigeration grade material. Most of the compounds were passed as vapor over Ascarite and phosphorus pentoxide, and then triply distilled in vacuum immediately before being placed in the thermometer. This latter procedure was intended to remove any traces of carbon dioxide, water, or inert gases.

EXPERIMENTAL WORK

Thermometer Design. Several different designs of the thermometer body are possible. Three of these, including Menzies' original design (6), are shown in Figure 1. The two proposed designs (B and C) have the advantage of a narrower cross-sectional area and, so far as the authors know, suffer no disadvantages over the original Menzies type (A, Figure 1). The length of the main capillary depends either on the ebullimeter to be used with the thermometer or the temperature differential to be covered. The length of the bulbs in turn is dependent on the length of the capillary, as they need be only large enough to contain liquid to fill the capillary. In most of this work the capillary was 18 cm. long, and the bulbs had a capacity of about 1.5 ml. each. There was no difference in results with the three designs.

Filling Thermometers. Menzies (6) says little about his method of filling the water thermometers except that "permanent gas is removed by the process of boiling out. . . ." This method cannot be used to fill nonaqueous thermometers, however, as there must be no decomposable vapor present at the sealing point (G, Figure 2) during the sealing operation. The following procedure was developed and used to fill thermometers with a variety of liquids. It is necessarily detailed, because manipulative difficulties arose where some variations were tried.

The series of traps and drying tubes, shown in Figure 2, was attached to the vacuum bench. The degree of vacuum necessary is not known accurately, but almost certainly it should be better than 1 μ . The system should be "tight" enough to hold this vacuum without the pumps for 2 or 3 hours. Having achieved this condition, a blank thermometer body was sealed on the bench at point A. Tube E was filled with suitable chemicals for the removal of carbon dioxide and water (usually Ascarite and phosphorus pentoxide), and fastened to the line, using a resin to seal J₁. Stopcock S₂ was closed and S₂ and S₁ were opened. The small tube furnace was placed around the thermometer body, heated to 530° C., and maintained at this temperature for approximately 2 hours. The furnace was then shut off and, after 15 or 20 minutes, removed from around the thermometer.

The desired amount of filling liquid was placed in tube F, frozen, and attached to the bench at J₂ with a resin sealing com-

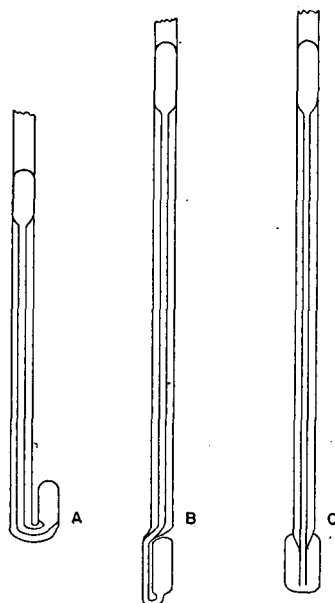


Figure 1. Possible Differential Thermometer Designs

A. Menzies original design
B, C. Proposed designs

pond. With the material in F still frozen, S₂ was opened cautiously and most of the air was pumped off (to approximately 10 μ). S₂ was closed and the material in F allowed to liquefy. After refreezing, S₂ was opened and any released gas was pumped off. This offgassing was repeated at least twice. Trap D was cooled with liquid nitrogen and the majority of the material in F was allowed to evaporate through E into trap D. When sufficient material had distilled over, S₂ was closed and trap C cooled. Trap D was allowed to warm up. When all the material had distilled from D to C, B was cooled and the material distilled into this trap.

With all the material in B, S₁ was closed and the contents of B were allowed to warm up. The thermometer body (which should have been at room temperature) was cooled with a refrigerant which did not freeze the filling material. (If such a refrigerant is not readily obtained, the filling is possible with a refrigerant that freezes the liquid, but is much more difficult.) When the thermometer body was filled to the desired extent, the material was frozen in place in the lower bulb and at the same time the unused material was frozen in trap B, C, or D. (This is a relatively difficult operation, and some experience is necessary to do it satisfactorily.) S₁ was opened and the system allowed to remain on the pumps 10 to 15 minutes. With a small flame, 1 to 2 cm. of the capillary were collapsed slowly just above the upper bulb and the sealed area was carefully annealed. The material in the thermometer was kept frozen until the seal cooled to room temperature.

As soon as the sealing was complete, S₁ was closed, S₂ and S₃ were opened, and the cooled trap was allowed to warm up. F was cooled with liquid nitrogen and kept cold until all the unused material had passed through E into it. Then S₃ was closed, F disconnected, and the remaining material discarded. S₁ was opened and the system pumped clean in the usual manner. With care, very little material ever passed through S₁ into the main bench.

The amount of liquid distilled into the thermometer was controlled carefully, so that enough liquid was present to fill the entire capillary at the lowest temperature at which the thermometer was to be used, and the amount of liquid present was somewhat less than the volume of either bulb. Otherwise, in the first case, the full length of the thermometer could not be used, while in the second case, the vapor space in the upper or lower bulb disappeared under certain conditions and the thermometer failed to operate. (In judging the amount of cooled liquid in the thermometer, its expansion upon heating must be considered.) Experience with differential thermometers is the best guide to their correct filling.

Sensitivity of Differential Thermometers. As Menzies (6) has pointed out, the theoretical basis for the differential thermometer's sensitivity is the small difference in the temperature of the two bulbs; this causes a difference in vapor pressure between the two arms of liquid which is registered as a substantially linear height function. The sensitivity of a thermometer depends entirely, therefore, on three factors: the vapor pressure-temperature differential of the filling liquid, the density of the filling liquid, and the average temperature of the two bulbs.

Menzies has calculated the sensitivity of the water thermometer over a range of temperature from 30° to 102° C. Unfortunately, data such as Menzies used for water do not exist for most organic liquids, but reasonably accurate calculations can be made from existing data. A recently published set of tables from

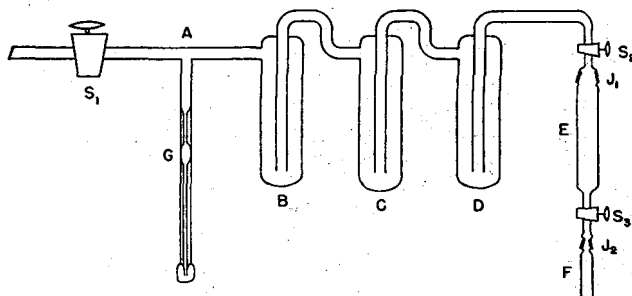


Figure 2. Vacuum Bench for Filling Differential Thermometers

Table I. Sensitivity of Differential Thermometers

T, ° C.	(Sensitivity, ° C. per mm. × 10 ³)						
	n-Pentane	n-Hexane	Benzene	n-Heptane	Water	Toluene	p-Xylene
30	2.07
36.1	1.72 ^a
40	1.55	24.7
50	1.19	3.20	6.03	...	15.8
60	0.93	2.40	4.44	...	10.4
68.7	...	1.88 ^a
70	0.74	1.82	3.34	...	7.1
80	...	1.46	2.56	3.28	5.0
80.1	2.48 ^a
90	...	1.13	2.00	2.50	3.56	4.46	...
98.4	2.02 ^a
100	1.59	1.95	2.60 ^a	3.43	...
110	1.54	1.92	2.68	...
110.6	2.63 ^a	...
120	1.24	1.46	2.25	4.58
130	1.13	1.71	3.60
138.4	2.95 ^a
140	0.88	...	2.86
150	0.70	...	2.30
160	0.56	...	1.87

^a Sensitivity at boiling point of filling liquid.

the National Bureau of Standards (1) gives constants of many organic liquids for the Antoine equation (A).

$$\log_{10} p = A - \frac{B}{C + t} \quad (1)$$

where p is the vapor pressure in millimeters of mercury, and t is the temperature in °C. A , B , and C are constants for any given liquid.

Differentiating this equation gives:

$$\frac{dt}{dp} = \frac{(C + t)^2}{B \times p} = \frac{\log_{10} C (C + t)^2}{B \times p \log_{10} C} \quad (2)$$

Division of the dt/dp value by $\frac{\text{density of Hg (0° C.)}}{\text{density of liquid (t° C.)}}$ gives the sensitivity of an organic liquid-filled thermometer. Table I shows the sensitivities of thermometers filled with different liquids between 30° and 160° C. and indicates that, for any given operating temperature, greater sensitivity can be obtained by using thermometers filled with lower boiling materials.

However, in molecular weight determinations a knowledge of the thermometer constant is not necessary. The authors have found experimentally that a scheme of comparative measurements, similar to that proposed by Swietoslowski (9), gives more accurate results by ruling out a number of small variables. The molecular weight in this case is based on the following equation:

$$m_u = \frac{w_u m_s \Delta t_s}{w_s \Delta t_u} \quad (3)$$

where m_u and m_s are the molecular weights, respectively, of the unknown and an added known, w_u and w_s are the weights of unknown and standard, and Δt_u and Δt_s are the observed temperature increases. As long as both are expressed similarly, Δt_u and Δt_s can be as readily expressed in millimeters as in °C. This obviates a knowledge of the thermometer sensitivity as such.

Attempts to Increase Sensitivity of Differential Thermometer.

One of the prime objectives of this work was to seek a method of increasing the differential thermometer sensitivity. Inspection of Table I shows that, at the boiling point of the filling liquid, the thermometric sensitivity is of the same order of magnitude for all the liquids listed, and they would be even closer if differences in liquid density were removed. However, another possible approach was the use of the thermometer at temperatures above the boiling point of the filling liquid. Superficially there are only two limitations to such a scheme: the pressure which the glass body would withstand and the critical point of the liquid.

Table I shows the sensitivity of a water thermometer from 40° to 180° C. [The data at 100° C. and below are from Menzies (8), the data above 100° C. are calculated from the usual vapor

pressure tables for water.] However, attempts to achieve these theoretical values experimentally with water between 130° and 180° C. have failed so far. Good checks were attained at 118° C., using glacial acetic acid as the ebulliometric liquid. Above about 130° C., corresponding to an internal pressure of 3 atmospheres, the zero reading of the thermometer was at the top of the capillary and the thermometer became useless. Even at lower temperatures, it had been noticed that the zero reading was considerably higher than predicted by capillarity, although this was not a source of trouble up to 118° C., at which temperature several centimeters of clear stem still remained. Similar phenomena were observed with thermometers filled with *n*-pentane, benzene, and toluene. The point at which individual thermometers became useless varied slightly but was at a temperature corresponding to 2 or 3 atmospheres internal pressure. No explanation of the phenomenon is readily apparent.

In only one case were the authors successful in using a differential thermometer at internal pressures over about 3 atmospheres. Two thermometers filled with sulfur dioxide operated reasonably well at 35° C., and one of them was taken to 80° C. without undue increase in the zero point. At the lower temperature, the theoretical sensitivity of 8×10^{-4} °C. per mm. was approached. Even at the lower temperature, however, the thermometer was slow in reaching equilibrium, presumably owing to the internal pressure of 5.3 atmospheres, and was not usable as an analytical tool under these conditions.

On the strength of these experiments, further work along this line was abandoned. No practical method is apparent at the present time for increasing greatly the sensitivity of a differential thermometer. In order to cover the range of ebulliometric solvents usually encountered with maximum sensitivity, it was decided to use a series of thermometers. The thermometers used to cover the range of 30° to 160° C. are listed in Table I.

These thermometers have been used for some time in the routine determination of molecular weights. The ebulliometer, thermometers, and technique, with typical results, are discussed in a second paper (5).

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Modified Menzies-Wright Ebulliometer for Molecular Weight Determinations

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The basic ebulliometric technique of Menzies and Wright for the determination of molecular weights has been modified to permit more rapid, precise determinations on a wide variety of materials. The use of differential thermometers filled with liquids other than water at temperatures above their normal boiling points permits greater precision over a wider range of solvents than is possible with the water thermometer. A modified ebulliometer is described which incorporates the improvements of previous workers in the field, together with a newly designed boiler and pump and which permits determination, precise to about 1%, in about 1 hour per sample.

THE method of Menzies and Wright (8) for the determination of molecular weight by the increase in the boiling point of a liquid is a well established technique and has been used, with some modifications, in this laboratory for a number of years. In the course of this work, and particularly after the development of the organic-filled differential thermometers described in the preceding paper (6), the ebulliometer has been redesigned in order to increase the speed, precision, and accuracy of the determination. This paper describes the ebulliometer as finally evolved, and presents typical data obtained with it.

The ebulliometric technique is thoroughly established, but the method has involved a rather large number of variables, the exact control or measurement of which was necessary to provide accurate results. By measuring the instantaneous difference in the boiling point of the pure solvent and the boiling solution, the differential thermometer of Menzies (7) removed, among other things, the effect of barometric pressure changes in the course of a determination. Subsequent investigators (1, 2, 4, 9) have not attempted to change the procedure of Menzies and Wright (8) greatly. All (except Barr and Anhorn, 1) used the water thermometer, converted the millimeter reading thus obtained to degrees Centigrade by Menzies' chart (7), measured the volume of solution at the boiling temperature, and employed carefully purified solvents. Although these investigators claimed a general precision of 1% for the procedure, the authors rarely have been able to achieve such reproducibility using the various published modifications. Examination of the details of the method suggested that the addition of a known standard immediately before and after the addition of each portion of unknown might permit substantial improvements in the procedure; the effects of changes in the purity of the solvent, volume of the boiling liquid, boiling rate, and other variables would be minimized, because the unknown would be measured in terms of a known standard. (This general technique has been proposed by Swietoslawski, 10). The molecular weight may be calculated by the relatively simple equation

$$m_u = \frac{w_u \times m_s \times \Delta t_s}{w_s \times \Delta t_u} \quad (1)$$

where m_s and m_u are the molecular weights of unknown and standards, respectively, Δt_s and Δt_u are the observed temperature change of known and unknown, and w_s and w_u are the weight of standard and unknown added. The main sources of error remaining in such a procedure, in addition to the four variables in the above equation, are those due to the change in the boiling rate and volume during a given series of determinations, and to interactions among solvent, standard, and unknown. The boiling rate and volume are readily controlled. Errors due to chemi-

cal reaction are usually of such magnitude as to be apparent to the operator or, in case of doubt, a rerun with radical changes in solvent and standard material quickly indicates whether reaction has taken place.

EXPERIMENTAL WORK

Apparatus and Chemicals. The ebulliometer in which most of the data given below were obtained is indicated in Figure 1. Two instruments were actually used. Although minor constructional differences existed between them, the accuracy and precision of the results were substantially identical.

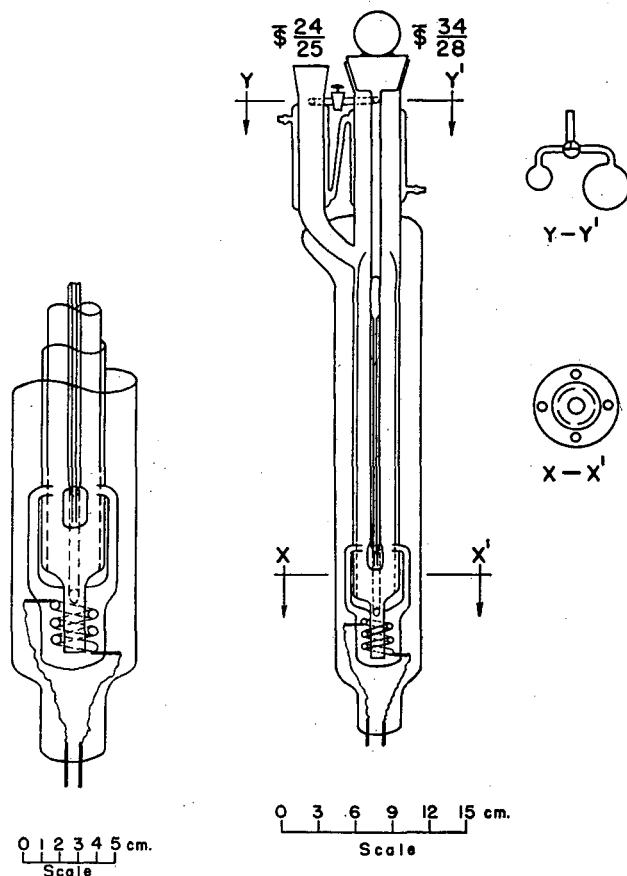


Figure 1. Modified Menzies-Wright Ebulliometer

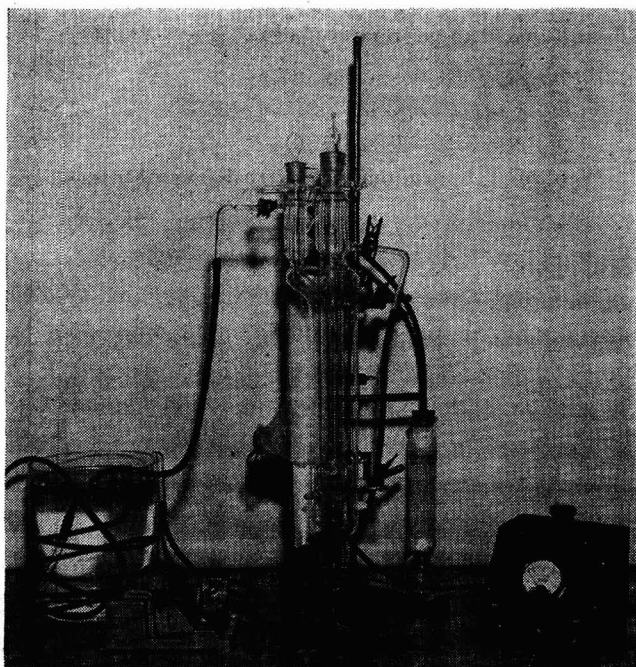


Figure 2. Ebulliometer and Auxiliary Components Assembled

The ebulliometer consists of a 30-ml. boiler in which an electrical heater, made of 225 cm. (7.5 feet, 50 ohms) of No. 30 Nichrome wire, is suspended, wound on a glass helix, and spot-welded to tungsten wire, which is sealed through the walls of the boiler. A second pair of tungsten leads, connected to the first by flexible nickel leads, provides the external contacts for the heater. At the top of the boiler, four integral pumps are so installed that all the vapor produced must pass through them, forcing a steady mixture of vapor and solution over the lower bulb of the thermometer. The pumps are constructed of glass tubing 5 mm. in outside diameter, each with unobstructed tip about 3 mm. long extending into the thermometer chamber. Condensed solvent returns to the boiler through a glass tube running through and under the heater. A rapid and efficient circulatory system is thus provided, which permits the instrument to reach equilibrium quickly after additions of solute.

The differential thermometer is suspended in the main chamber of the ebulliometer, so that the lower bulb is just below the level of the pump jets. The thermometer is surrounded by an inner mantle, which serves to protect it from the returning condensate, and from portions of solute which otherwise might lodge on the stem. This mantle is slotted to drop over the pump jets, and may be removed through the main condenser to facilitate cleaning of the thermometer chamber. Just above the upper bulb of the thermometer, a side arm enters the thermometer chamber and is used for sample additions. The top of the sample arm is closed with a $\frac{1}{4}$ 24/25 joint and stopper. The thermometer is mounted on a $\frac{1}{4}$ 35/28 joint at the top of the main arm of the ebulliometer. An 8-mm. tube near the top of each arm is connected to a T stopcock, which is fastened to a drying tube that dries all the air "breathed" during a normal run.

Cooling water for the condensers is circulated by a small pump from a simple thermostat, constant in temperature to $\pm 1^\circ\text{C}$.

The heater is connected, through an ammeter, to a variable-voltage autotransformer. With a 50-ohm heater, between 1 and 2 amperes normally are used. The transformer, ammeter, and pilot light are all mounted in a small metal box, together with an "Off-On" double-pole single-throw switch which supplies current to both the transformer and the circulating pump motor.

Thermometer readings (liquid levels) are made most satisfactorily with a cathetometer. A small Lumiline or fluorescent lamp is mounted vertically in back of the ebulliometer to aid in reading the thermometers.

Two sets of differential thermometers were used, each set containing, respectively, benzene, toluene, *p*-xylene, *n*-pentane, *n*-hexane, and *n*-heptane; they were constructed and filled by the methods described in the previous paper (6).

The ebulliometric solvents were c.p. materials, used as purchased, except that the aromatic solvents were dried over sodium metal.

The molecular weight standard most frequently employed was benzil (Eastman Kodak Co. No. 35, molecular weight 210.22). The purity of the material was assumed to be 100% after samples of recrystallized material, used as standard, gave a molecular weight value of 210.1 for the c.p. compound as received (Table I). (Some care obviously must be used at this point; new batches of standard should be checked against old before use.) The material was pelleted into 100-mg. pills with a small press. Other satisfactory standards include hexamethylbenzene, hexaethylbenzene, naphthalene, and anthracene.

Solid samples were pilled before addition to the ebulliometer. Liquids were added from a weight buret.

Procedure. Before analyzing a sample, the operator must decide what solvent and what differential thermometer are to be used. The nature of the solvent is dependent entirely upon the sample, and no general rules are laid down here for its selection except that the solvent should boil at least 150°C . below the solute. Having chosen the solvent, the choice of the thermometer is relatively simple. For average sensitivity, a thermometer filled with a liquid having a boiling point equal to or slightly less than that of the solvent should be used. For the maximum sensitivity, as when materials of high molecular weight are being analyzed, a thermometer filled with liquid boiling as much as 20° or 30°C . below the ebulliometric solvent may be chosen. Thus when benzene or carbon tetrachloride is used as solvent, a benzene thermometer should be used for average sensitivity, while a thermometer filled with *n*-hexane or acetone will provide greater sensitivity.

In making a molecular weight determination, the ebulliometer and its auxiliary components are assembled as shown in Figure 2.

Pipet 30 ml. of the ebulliometric solvent through the sample side arm, insert the desired thermometer in the main arm, and put a stopper in the sample arm. Turn on the condenser water and the heater current, setting the latter to the desired value. (If this has not been determined previously, increase the amount of current slowly until the boiling rate is sufficiently high to give good pumping action, but not high enough to force liquid back through the return tube into the compartment around the lower thermometer bulb.) When the condensation level has reached the condensers, note whether there is free vapor space in each of the thermometer bulbs. Not infrequently the high differentials, encountered in first boiling the liquid, will force all the thermometer fluid into the upper bulb. If this has happened, lift the thermometer about 1 cm., and tap it lightly until a vapor space is obtained in the upper bulb. (In properly constructed thermometers this should not be a source of difficulty.)

If the thermometer is well filled, the initial reading probably will be in the stem enclosed in the lower thermometer bulb or just at the ring seal. In this event, add a small quantity of the standard material (25 mg. of benzil are sufficient) to force the liquid into the long capillary above the ring seal. Allow the instrument about 10 minutes to reach equilibrium after the condensation level becomes constant. Then check the thermometer reading every 2 or 3 minutes until constancy is obtained. Ordinarily it is necessary to read only the height of the liquid in the long capillary arm. When the thermometer reading is constant, add a weighed pellet of the standard material through the sample arm. Allow the instrument from 5 to 10 minutes to equilibrate again, and note the second liquid level in the thermometer. Then add the weighed portion of sample, and repeat the temperature reading after equilibrium is regained. Continue the alternate additions of weighed portions of standard and sample as long as desired or until the liquid in the thermometer capillary comes within 2 cm. of the upper bulb of the thermometer. Experience with the apparatus and the various types of samples will tell whether only a single sample or several different consecutive samples may be run in a given portion of boiling fluid. In the authors' laboratories, both approaches are used.

After the last temperature reading has been made, shut off the heater current and the condenser water. Remove the solution from the ebulliometer with a small, glass-tipped suction line. Rinse the apparatus with one or two portions of solvent, and proceed with the next series. If a different solvent is to be used, several rinses with the new solvent will be needed before making the run.

Calculations. Only four experimental values are needed to calculate a molecular weight: the weight and subsequent change of temperature (expressed conveniently as millimeters rise in the

capillary arm of the thermometer) for a pellet of standard and the corresponding data for a pellet of unknown. Obviously, weight and temperature differences must be expressed in the same respective units, but the character of these units is unimportant. Substitution of these values, together with the molecular weight of the standard, in Equation 1, will permit the calculation of the unknown molecular weight. It is usually desirable to add a pellet of standard both before and after the addition of the sample; in this case, the standard data can be averaged before substitution in the formula.

If a number of standard and sample additions are made, it is convenient to calculate a K value for the standard, and then use this value in the subsequent calculations.

$$K = \frac{m_s \times \Delta t_s}{w_s} \quad (2)$$

These K values are calculated for a single run. If they show good random agreement, they are averaged, and the molecular weight of the unknown is computed for each addition of unknown, as follows

$$m_u = \frac{K \times w_u}{\Delta t_u} \quad (3)$$

If a trend is obvious between K values, two successive values are averaged and used to calculate the sample run between them. The operator must seek the cause of the trend, and recognize a possible decrease in accuracy and precision in this case.

When a large number of similar samples are to be run using the same solvent, the same ebulliometer, and the same thermometer, and when the best accuracy is not required, the value for K can be established by a suitable number of calibration runs, and then assumed to remain constant. Its value can be checked at intervals. If this procedure is used, the controllable variables, such as condenser water temperature, boiling rate, solution volume, etc., must be maintained as constant as possible.

EXPERIMENTAL RESULTS

Because of the established nature of the ebulliometric procedure, no special work has been done with the modified apparatus to check the molecular weights of known compounds. The data in Table I are typical of the results obtainable. These materials were analyzed in the same manner as routine samples, generally with triplicate additions during separate runs on the individual substances.

Table I. Typical Results with Knowns

Known	Reference Standard	Solvent	Thermometer	Molecular Weight	
				Known	Found
Benzil (C.P. as received)	Benzil (recrystallized)	Benzene	Benzene	210.2	210.1
Benzil (machine pelleted)	Benzil (hand pelleted)	Benzene	Benzene	210.2	210.0
Azobenzene	Benzil	Carbon tetrachloride	Benzene	182.2	183.1
Cyclopentyl-3,5-dinitrobenzoate	Benzil	Benzene	Benzene	280.3	282.1
Heptadecanol	Benzil	Carbon tetrachloride	Benzene	256	254
<i>n</i> -Cetane	Benzil	Benzene	Benzene	226.4	224.1

The data in Table II, which indicate the precision of the method, were obtained as follows.

The ebulliometer was operated in the manner described above. The solvents and thermometers listed were inserted into the apparatus, and then successive weighed portions of a known standard, usually benzil, were added, and the resulting rises in temperature were noted. From these data the value, milliequivalents per millimeter of thermometer liquid rise, was calculated. At least six portions of standard were added. The probable error of a single value, and the probable error of the mean, were then cal-

culated according to familiar statistical procedures, and these values converted to per cent of the average. Table III shows a similar set of data, obtained for a series of unknown samples on which six or more values were obtained.

Table II. Reproducibility with Known Material

Solvent	Thermometer Liquid	Probable Error, %	
		Single value	Mean
Benzene	Benzene	0.6	0.3
	Hexane	1.7	1.0
	Benzene	4.1	1.6
Carbon tetrachloride	Heptane	0.7	0.2
	Toluene	3.4	1.4
	Heptane	1.9	1.0
Toluene	Heptane	3.3	1.7
	Toluene	3.8	1.1
Xylene	Xylene	Av. 2.4	1.0

The samples analyzed to date have generally been run in triplicate, and hence do not lend themselves readily to statistical study. The following treatment was made of data covering about 150 samples, run consecutively. The deviation from the mean was calculated for each of the three values in the sample, and from this the average deviation was obtained. This value was converted to per cent of the average. For 120 consecutive samples this average deviation ranged from 4.7 to 0.1%; the average was 1.5%. In the course of running these samples, the value of K (Equation 2) was recorded, to give some indication of the precision obtainable by establishing this value, and then omitting the standard addition during each individual run. Table IV summarizes these data.

Table III. Reproducibility with Unknown Materials

Sample No.	Molecular Weight Found	Probable Error, %	
		Single value	Mean
1	315	3.2	1.4
2	432	3.1	1.2
3	416	2.4	1.1
4	471	2.6	1.1
5	450	2.5	1.0
6	296	1.4	0.6
7	254	1.7	0.7

Experience with the ebulliometer has shown that one operator can analyze seven or eight routine samples in triplicate per 8-hour day. This allows time for sample pilling (if necessary), calculating and reporting results, and the necessary cleanup. Completely unknown samples require longer times, depending somewhat upon the operator's skill in selecting suitable solvents, thermometers, etc., without undue experimentation.

The instrument has been used on samples boiling as low as 200° C., and on polymeric materials with apparent molecular weights as high as 2500. The accuracy of the instrument for these materials of high molecular weight has not been established definitely, but precision between results on such samples, while lower than those obtained on lower molecular weight samples, does not appear to be inconsistent with the lack of homogeneity and low solubilities of such samples, and the probable errors in measuring very small temperature differences.

DISCUSSION OF RESULTS

Ebulliometer Design. Before designing the present apparatus, considerable development work was undertaken on the various components. The experience of others was reviewed, and certain features, such as the vacuum jacket and the immersion electrical heater, were adopted directly. The development of thermometers filled with nonaqueous liquids has been presented in a previous paper (6). These new thermometers, and the techniques developed to handle them, permitted liberties with

Table IV. Variation of Value of *K* for a Benzene Thermometer

Ebulliometer No.	Solvent			
	Carbon Tetrachloride		Benzene	
	<i>n</i>	Av. deviation, %	<i>n</i>	Av. deviation, %
2	176	1.3	43	1.4
3	27	3.1	92	1.4

n = number of runs.

the ebulliometer design which were not available to previous workers in the field.

The principal changes in the ebulliometer involve the boiler, heater, and pumping arrangement. After testing numerous designs, the removable pumps used previously were abandoned in favor of the sealed-in design. Two-, three-, and four-jet arrangements were tried, the last giving the best combination of pumping speed and ease of glass blowing. One ebulliometer was constructed in which the 3-mm. tips on the jet end of the pumps were omitted. Lack of these tips did not seem to affect the results obtained with the instrument, but the solvent running down the sides of the thermometer chamber obviously interfered with the pumping action. Except for their diameter, the pump arm dimensions did not appear to be critical.

A number of different styles of heaters were tried. The boiling rate appeared to be a simpler function of energy input, if the heater was completely surrounded by the boiling liquid, or was mounted on a small, glass helix. (The latter design is the more rugged, and is preferred.) Heaters mounted on a relatively large support showed a tendency towards lower boiling rates for a given energy input. No decomposition of the solvents mentioned in this paper or a wide variety of solutes has been observed on the Nichrome heaters over 18 months of operation.

Enclosing the top of the apparatus, to prevent the introduction of moisture into the ebulliometer during a run, was necessary primarily in order to permit determinations in humid weather. The side arm permitted the addition of sample without disturbing the thermometer.

The chief disadvantages are the inconvenience and expense involved in replacing the heater wire, in the event of a burnout, and the difficulty of cleaning the boiler. The latter could be reduced by the use of platinum instead of Nichrome wire for the heater, but this in turn makes the heater more susceptible to burn out.

Ketchum's (5) method of mounting the heater on a glass joint was published after the development of the ebulliometer here described. Although its adoption in the present ebulliometer was seriously considered, no models containing it have yet been made, because a comparatively large grind would be required for the authors' device with the attendant increased possibility of leakage. However, they plan to try Ketchum's arrangement in a further development of their apparatus.

The present procedure calls for reading the change in temperature, upon the addition of a pellet of solute, only as the change in the height of the liquid in the capillary arm of the thermometer. However, the level of liquid in the lower bulb also changes as the level in the capillary changes (because the total volume is constant). In a well constructed thermometer this change is linear, and a small, constant correction should be added to the change of liquid level in the capillary arm to give the true change in height. Actually, this is unnecessary in this procedure; since the error term is essentially equal for successive thermometer readings and cancels out in the Δt_s and Δt_u terms in Equation 1. As dt is small (ca. 0.01° C.), dp/dt is assumed to be linear.

One feature of all previous equipment, which is completely omitted in this design, is the small metal clip, originally recommended by Menzies and Wright (8), for conducting condensed solvent from the condenser wall to the upper stem of the thermometer. The authors have found that this arrangement fails to

achieve its objective of stabilizing the thermometer reading. Among the substitutes tried, the most successful was a small cold-finger condenser, to the bottom of which the thermometer was attached; this device has also been reported by Colson (3). The cold finger was used for some time on all thermometers and seemed to increase the thermometer stability. After several months of routine operation, however, circulation of liquid through this condenser was discontinued without apparent effect on the stability of the thermometer. The authors have no explanation for this apparent anomaly.

Analytical Results. The chief concern in the development of the present ebulliometric method was the need for a rapid, relatively precise procedure for the determination of the molecular weights of a wide variety of samples. In general, it was desired to establish this value to 1%. Greater accuracy is of little value in establishing the nature of pure compounds or polymeric materials of low molecular weight. Consequently, no great effort was expended to refine the method to give more precise results, although this probably could be done.

On one occasion it was desired to establish very definitely the molecular weight of a compound, and three independent sets of triplicate values were obtained. The difference between the average value for the nine results and for the average of any set of three determinations was considerably less than 1%.

Of the solvents and thermometers used, the benzene combination has been the most generally useful. Benzene is a highly versatile solvent, easily obtained in a high degree of purity; it boils smoothly, and has good ebullioscopic constants. The benzene-filled thermometer is generally used with benzene, although the *n*-hexane thermometer will give greater sensitivity. As a companion solvent, for materials not readily measured in benzene, the authors most frequently use carbon tetrachloride with the same pair of thermometers. Materials of very high molecular weight are run in xylene with either the *p*-xylene or toluene thermometer. Other solvents, such as ethanol, 1-propanol, ethyl ether, and toluene, have been used successfully.

The authors have not been able to obtain known materials of very high molecular weight, and hence are unable to verify the accuracy of the present procedure for such materials. Extensive data on samples, ranging in molecular weight from 1000 to 2500, indicate a fairly good precision, although not so good as at lower molecular weights; this, however, is not inconsistent with the known inhomogeneity of such samples.

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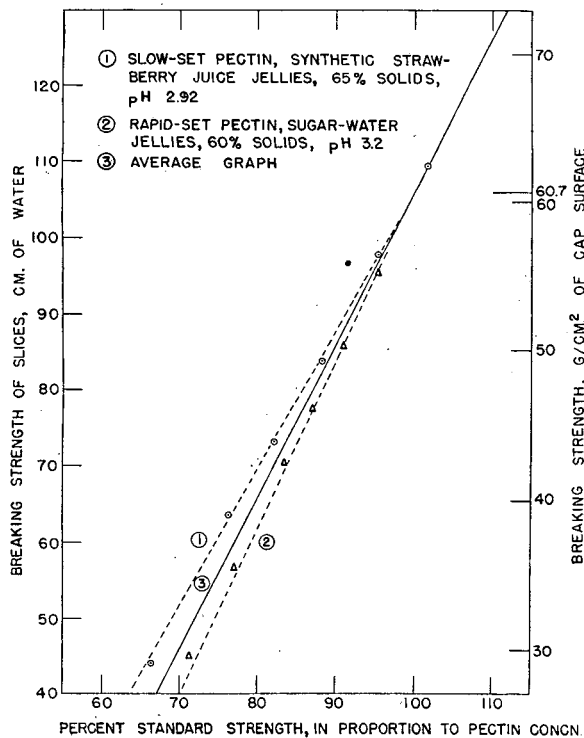


Figure 2. Standard Graph for Pectin Grading

A diagram of the apparatus used is given in Figure 1.

The manometer column of the Tarr-Baker gelometer (Arthur H. Thomas & Company, Philadelphia 5, Pa.) is lengthened to about 145 cm. Air at constant pressure (Nullmatic pressure regulator, Model 40-50, Moore Products Company, Philadelphia 24, Pa.) in the range 2.1 to 2.25 kg. per sq. cm. (30 to 32 pounds per square inch) passes through an adjusted needle valve (No. 309 V-point needle valve, 0.25-inch, Hoke, Inc., Englewood, N. J.) to the pressure chamber of the instrument, thence through a plug of cotton to the syringe and water manometer. The pressure regulator, which is protected by an efficient drip well and air filter, is placed close to the gelometer for convenience in adjusting the pressure. Between the needle valve and the gelometer is inserted a mercury manometer, as a safety valve, to blow out at 20 cm. The plug of cotton acts as a constriction in the line, causing the rising manometer column to dip at the instant of break and to dampen the return flow of air between slice readings. The instrument is trued up so that the platform is level and the piston cap rests square on the wood block that holds the slices.

Speed of Manometer Rise. With the pressure content at 31 pounds per square inch, the needle valve is adjusted by trial until, when the air outlet is closed, the column rises at a speed of 100 cm. in 46 ± 0.5 seconds, measured from 10 to 110 cm. Once adjusted, and after reaching equilibrium, no further change is made in the needle valve, but further small adjustments to secure correct speed, are made by slight changes in the air pressure within the range of 30 to 32 pounds per square inch. Such pressure is necessary to maintain a nearly constant rate of rise over the whole manometer column. The speed should be checked at intervals of 2 to 3 hours. Variations of ± 2 seconds per 100 cm. will entail errors of approximately $\pm 1\%$ in grade determinations.

Determination of Slice Strength of Jellies. Allow jellies to stand 18 to 24 hours at room temperature. Cool jellies before testing, so that the slices, when tested, will be at 20° C. Unmold jelly and cut slices 6 to 7 mm. thick beginning at bottom of jelly. Discard the bottom slice. Using a spatula, place the next four slices in rotation on paper about 12.5 cm. square. To avoid breaking or cross-cutting the slices, use a spatula with a blade 10×1.8 cm. having slightly rounded edges. Measure thickness with slices lying flat on their paper support. Slices as thin as 5 mm. or as thick as 8 mm. will give readings somewhat out of line.

Close the air outlet of the gelometer and transfer paper with slices to block under piston, holding piston at neck with tongs. Center the first slice under piston and allow cap to rest on it.

Observe top of column. At the breaking point there is a definite stop and a slight drop. Record reading to nearest centimeter. Open air outlet valve, raise piston, rotate next slice into place, and allow cap to rest on it. Close outlet valve at once and take readings on this and remaining slices in the same way. Thus, each slice starts at a manometer reading of about 20 to 25 cm. Repeat with a second glass. Average the readings for each glass. If the glasses average as much as 4 cm. apart, run a third glass. Calculate the average slice strength from the glass averages.

Procedure for Grade Calculation. The derivation of the graph, Figure 2, and the development of the suggested standard of strength are given in detail under experimental data below. The use of the breaking strength of slices in the grading of pectin may be shown by an example.

Assume that a jelly containing 356 grams of sugar and 2.00 grams of pectin was found to have 106-cm. breaking strength and that the syringe had been calibrated and found to require no correction. By reference to Figure 2, the jelly is found to be 100% standard and the grade is at once obtained by dividing the sugar weight by the pectin weight, giving 178. A second jelly containing 356 grams of sugar and 1.80 grams of the same pectin had a breaking strength of 82 cm. or 88% standard by Figure 2. If the second jelly were now made with 12/88 increased pectin concentration, but otherwise identical, it would be 100% standard. The grade for the second jelly will therefore be given by the expression:

$$\text{Grade} = \frac{356 \text{ grams of sugar}}{\frac{100}{88} \times 1.80 \text{ grams of pectin}} = \frac{88\% \times 356}{1.8} = 174$$

The grade is taken as the average of the two determinations or 176.

The proposed graph (Figure 2) may be represented by the approximate equation, in slope-tangent form, $y = 2x - 94$ or $x = y/2 + 47$, where x is the pectin concentration as per cent standard and y is the breaking strength in centimeters. It is, therefore, simpler to calculate the per cent standard as follows, than to refer to the graph:

$$\text{Per cent standard} = \frac{\text{breaking strength}}{2} + 47$$

$$\text{Pectin grade} = \frac{\% \text{ standard} \times \text{sugar weight}}{\text{pectin weight}}$$

Calibration of Gelometer Syringe. The difference between the diameters of the piston and the cylinder should be from 0.0175 to 0.0375 mm. (0.0007 to 0.0015 inch) to minimize sticking and air leak, respectively. Satisfactory dimensions are: cylinder diameter 1.45 cm. (0.5700 inch), cap diameter 2.03 cm. (0.800 inch), weight of piston 21 grams.

In Figure 2 a jelly of 100% standard is taken as breaking at a pressure of 60.7 grams per sq. cm. of cap surface. The manometer reading at which this standard pressure is obtained is not necessarily 106 cm., as given in Figure 2, but depends on the dimensions of the syringe used. To use Figure 2 with another syringe it is necessary to apply a correction factor to the strength as per cent standard or to the final grade. This correction is determined as follows:

Obtain the average inside diameter of the cylinder about one third down from the top with a micrometer gage and calculate the average cross section in centimeters A . Take the average diameter of lower quarter of cap and calculate area in centimeters, B . Weigh piston, C .

$$D = \text{air pressure thrust, grams per sq. cm. of cap area per cm. rise in manometer} = \frac{1 \text{ gram per sq. cm. per cm.} \times A}{B} \text{ gram per sq. cm. per cm.}$$

$$E = \text{piston thrust} = C/B \text{ grams per sq. cm. of cap area}$$

$$F = \text{calculated manometer reading for 100\% standard} = \frac{60.7 \text{ grams per sq. cm.} - E}{D} \text{ cm. (if a different standard of strength were adopted, the figure 60.7 would change accordingly)}$$

$$G = \text{apparent \% standard, by graph, corresponding to } F \text{ cm.}$$

$$\text{Correction for high readings} = -\frac{G - 100}{G} \%$$

If a syringe correction is less than 2%, the corrections for high and low readings are nearly the same, but if the correction is as great as 5% the corrections for high and low readings will differ as much as 1.4% and may be scaled accordingly. A convenient correction point for low readings is at 72% standard (50 cm., Figure 2) where the standard pressure is 32.1 grams per sq. cm. of cap surface. The calculated manometer reading for 72% standard is therefore (32.1 grams per sq. cm. - E)/ D , and the correction is calculated as above.

Care of Syringe. To clean thoroughly, the syringe is washed with Lava soap, rinsed well in tap and distilled water, and dried in air. It is lubricated with a thin film of grease obtained by rubbing the dry piston on clean skin. Any suspicion of sticking is checked at once. The cylinder is swabbed with wet cotton on a wire, then swabbed with 60% isopropyl alcohol, and dried quickly with the full flow of air. At the same time the piston is washed and lubricated.

EXPERIMENTAL DATA

Suggested Strength for Standard Jelly. In connection with the production of a concentrated extract of apple pectin, beginning in 1913, it became necessary to set a standard for its jelly value, later termed grade (20). A standard of jelly strength was established and maintained by successive lots of pectin kept in cool storage, later by comparison with competitive products, and by knowledge of the strength required for shipping and of consumer preference. Before instruments were devised the comparisons were made by expert finger testing of the breaking strength of jelly slices. When more than one laboratory became involved, expert finger tests became inadequate. The slices of standard jelly have been found to break with the syringe used and under the controlled conditions described above, at an average of 106-cm. water pressure on the Tarr-Baker gelometer. Measurements of the particular syringe used showed that the average breaking strength was 60.7 grams per sq. cm. of cap surface, which was checked by actual weighings of the thrust of the piston. This reproducible standard of strength has been used by General Foods since 1938 in the production of pectin for household and preservers use.

Development of Method for Determining Strength of Jelly in Terms of Standard. When a series of six jellies, in duplicate, of constant solids and pH value was tested, the graph of breaking strength vs. pectin concentration was a straight line. From the manometer readings and the syringe dimensions and piston weight the total pressures at each breaking point were calculated in grams per square centimeter of cap surface. These values, which checked closely with actual pressures by weighing the thrust, were also in straight-line relation to pectin concentration. If any specific breaking strength is selected as 100% standard, then the concentrations of pectin corresponding to 100% standard and to other percentages of standard may be calculated and the pectin concentrations may be restated as per cent standard, as shown in line 1, Figure 2.

The series just mentioned was made from slow-set pectin at 65.7% solids, pH 2.92, and in the presence of the metal ions provided by a synthetic strawberry juice (13). A second series was made under different conditions: rapid-set pectin concentrate, 60% solids, pH 3.2, and a low concentration of metal ions. The resulting graph, calculated to pectin concentrations expressed as per cent standard as above is shown in line 2, Figure 2. This agreed at the higher strengths with the slow-set type but gradually diverged until, for example, at a breaking strength of 45 cm. the corresponding standard strengths were 66.4 and 72.4%.

The average values for these two series were taken as best representing pectins of different types in jellies of different composition. Line 3, Figure 2, represents this average relation be-

Table I. Grades of Pectins in Pairs of Jellies of High and Low Strength, of Equal Solids and pH Values

Type	Pectin		Jelly			Pectin Grade	Grade Difference, High to Low Strength Jellies, %	
	Approx. equiv. weight ^a	Amount, grams	Medium	pH	Calcd. solids, %			Slice strength, cm.
Rapid set ^b , citrus	750	3.20 2.30	Water	2.98	68	102.5	116	+0.9
				2.99	68	47.6	117	
Medium set, orange	650	1.70 1.30	Synthetic (13) strawberry juice	3.20	65	76	178	0.0
				3.22	65	36	178	
Medium set, orange	650	1.70 1.30	Synthetic (13) strawberry juice	3.22	65	94	196	-2.5
				3.26	65	46.5	191	
Rapid set ^b , apple	400	3.30 2.10	Water	2.16	65	114.5	113	+0.9
				2.14	65	39.2	114	
Rapid set ^b , apple	400	3.00 2.10	Water	2.07	65	114.2	125	0.0
				2.05	65	51.7	125	

^a Apparent equivalent weight of acid-alcohol washed pectinic acids, including "ballast" material.

^b Commercial pectin diluted with dextrose by manufacturer, to reduce its grade to standard value.

tween pectin concentration, expressed as per cent standard, and the breaking strength of slices. The main assumption made was the selection of the specific breaking strength of 106 cm. to represent 100% standard. If a different standard should be selected, then from the present graph a new one can be calculated which will nearly parallel the present line and will be to the left or the right of it, depending on whether the new standard selected is stronger or weaker than the one here suggested.

Test of Linear Relation of Figure 2 for Various Types of Pectin. The test consisted in comparing the grades obtained for a pectin in two jellies, both of the same solids and pH values but of different pectin content. As shown in Table I, the grades of the pairs, computed as above, were in fairly close agreement. This tends to show that the linear relation between slice strength and pectin concentration given in Figure 2 is valid over a moderately wide range of pectin types and jelly conditions.

Precision. It is not practicable to report the accuracy of a method of this kind by direct test on samples of known value. Its precision was estimated from determinations made on five samples of pectin by several operators in two laboratories. On three of these samples, and on four others, pairs of duplicate determinations were also made. In one of the laboratories the gelometer syringe required a correction of +4.8%. The experience of the operators varied from slight to considerable. The jelly factors were standardized as follows: calculated solids 65%; pH 3.20 ± 0.03. Synthetic juice (13) was used as jelly medium; the pectin solution and synthetic juice were brought to a boil, sugar was added, and the whole was boiled to a net weight. Container size, Hazel-Atlas glass 883. The results are given in Tables II and III.

Table II. Precision of 41 Single Determinations by Several Operators in 2 Laboratories

Sample No.	Labs.	Operators	No. of Detns.	Range of detns.	Grades by Single Determinations		Coefficient of variation ^a (standard deviation, σ' , expressed as % of average, \bar{X}), %
					Average, \bar{X}	Standard deviation, σ'	
717	2	4	6	221-231	225		1.64
721	2	6	12	248-270	258		2.28
724	2	5	9	337-365	349.4		2.62
725	1	4	7	238-250	244		1.84
726	1	4	7	233-247	239.6		2.43

$$a \sigma' = \frac{1}{c_2} \sqrt{\frac{\sum (X - \bar{X})^2}{n}} \quad (\text{A.S.T.M. tables})$$

Inasmuch as the number of subgroups was small, the data were treated by the small sample version of the control chart method. An analysis of variance was not practicable because of lack of symmetry. Table II shows that the standard deviation of a single determination (expressed in percentage of the average) ranged from 1.6 to 2.6%; while for the 41 determinations the weighted over-all value of the standard deviation was 2.24%. The limits of variation for a single determination may be expressed as follows: One determination in about 20 may be expected to deviate from the average by more than 2σ or $\approx 4.5\%$; this actually occurred once in the 41 tests.

Table III. Precision of Duplicate Determinations

Sample No.	Grades by 2 Operators, Averages of Dup. Detns.	Av., \bar{X}	Coefficient of Variation ^a (Standard Deviation, σ' , Expressed as % of Average, \bar{X}), %
385 ^b	242, 232	237	3.74
395 ^b	266, 268	267	0.66
400 ^b	247, 251	249	1.42
405 ^b	247, 247	247	0.0
717 ^b	227, 222	224.5	1.98
725	242, 244	243	0.73
726	246, 239	242.5	2.56

$${}^a. \sigma' = \frac{1}{\sigma_2} \sqrt{\frac{\sum(X - \bar{X})^2}{n}} \quad (\text{A.S.T.M. tables})$$

^b Operators in 2 laboratories.

The standard deviation for seven pairs of duplicate determinations (expressed as percentage of the averages) ranged from 0 to 3.7%, with a weighted over-all value of 1.98%. This compares with a standard deviation of 1.58%, calculated from the value for single determinations ($2.24/\sqrt{2}$). This discrepancy is due to the first group in Table III with $\sigma' = 3.74\%$, which was obviously out of control.

The method described above has been in use in experimental and control work for a number of years in General Foods laboratories and is considered reliable. It will be found of value in experimental work where pectins may be compared with fair

precision under any desired conditions, whether the jellies be relatively weak or of ordinary strength. In production control, whether of pectin or preserves, it affords the manufacturer a reliable means of determining pectin grade by breaking strength, using either a set of jelly factors that may be adopted as standard or the particular jelly factors that apply to a given situation.

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Determination of Choline Chloride and Choline Citrate

By Means of Cadmium Chloride

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A gravimetric method for the determination of choline chloride and choline citrate is based upon the previously reported formation of an ethanol-insoluble complex compound of choline chloride and cadmium chloride, $(\text{CH}_3)_3\text{NCl} \cdot \text{C}_2\text{H}_4\text{OH} \cdot \text{CdCl}_2$. Values have a standard deviation of better than $\approx 0.1\%$. There is either no systematic error or at most an error of about -0.1% . The method may be used for the assay of pharmaceutical grade material and, with some limitations, for the determination of choline in crude samples obtained during production. It has not been investigated for biological samples.

CHOLINE chloride and choline citrate have come into prominence as medicinals, and suitable analytical methods have become necessary, both for assaying the finished products and as a means of control in their production.

A method given in the United States Pharmacopoeia (6) for the assay of choline chloride (when used as a reagent, not as a pharmaceutical) is based merely upon the chloride content of the substance. This is not specific for choline and cannot be used for the assay of the citrate nor for the determination of choline in crude preparations obtained during the course of production.

The Council on Pharmacy and Chemistry of the American Medical Association has also published tests and standards for choline dihydrogen citrate (5). The method of assay involves precipitation of choline as a reineckate and a spectrophotometric determination of the latter by the magnitude of the absorption of an acetone solution at 5260 Å (3). This method is in widespread use for biological samples, but its utility for the purpose of this study is limited by the fact that spectrophotometric methods in general do not have a precision better than 1 or 2 parts per 100 parts of the constituent being determined. A number of in-

investigators confirm this conclusion (2, 13, 14) and at least one points out the lack of specificity of the method (14).

Another type of method, which was also considered, involves the precipitation of choline as the periodide followed by the determination of nitrogen in the precipitated periodide (4, 10-12) or by an iodometric determination with sodium thiosulfate (?). This method is reported to have a maximum error of $\pm 5\%$ (?), and according to Thornton and Broome (13) is rather difficult to use, as it involves working with a very unstable compound and it gives low results when used as described by the author.

The method finally adopted was based upon the precipitation from ethanol of a complex compound of cadmium chloride with choline chloride, $(\text{CH}_3)_3\text{NCl} \cdot \text{C}_2\text{H}_4\text{OH} \cdot \text{CdCl}_2$. This compound was originally reported by Schmidt (8), who used it as a means of isolating choline chloride. Some experiments were made with a few other metallic chlorides as precipitants of choline. Mercuric chloride (1, 9), cobaltic chloride, and cupric chloride complexes had higher solubilities in ethanol than the corresponding cadmium chloride complex; and ferric chloride, lithium chloride, and nickel chloride showed no precipitation whatsoever.

The method described consists of precipitation of the cadmium chloride complex from an alcoholic solution of choline chloride and subsequent gravimetric determination. It can be applied to choline citrate by including hydrochloric acid in the solution of the sample and used for the determination of choline chloride (and presumably choline citrate) in crude preparations as well as in purified preparations. For crude preparations, however, the precipitated cadmium chloride complex should be analyzed for nitrogen before the results of the analysis are accepted. Low nitrogen values may be obtained for some crude samples, in which case the method would not be applicable without modification. The method has not been investigated for biological samples. The values obtained are precise, the standard deviation being less than $\pm 0.1\%$ for pure solutions, and the systematic error is not more than about -0.1% at the most. A conceivable interference in the determination would be betaine hydrochloride which, upon addition to samples of choline chloride, increased the values obtained by about one half or less of the amount of betaine hydrochloride added, but because betaine hydrochloride can be titrated as an acid, whereas choline chloride cannot, the presence of the former may easily be detected. There is no reason to believe that betaine hydrochloride would be present in the type of samples with which this study is concerned.

REAGENTS

Cadmium Chloride Solution. Anhydrous cadmium chloride is prepared by drying ground crystals ($\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$) in the steam oven overnight. (Purchased anhydrous material could probably be used.) An excess of the anhydrous salt is shaken with absolute ethanol, and allowed to stand for a few hours, with occasional shaking, and the solution is then filtered.

Transfer and Wash Solution. Absolute ethanol is shaken with some of the choline chloride-cadmium chloride complex, and the mixture is allowed to stand for an hour or so with occasional shaking, and filtered just before use.

PREPARATION OF SAMPLE SOLUTION

For choline chloride, a 4.0- to 4.5-gram sample is weighed by difference, transferred to a dry, short-stemmed funnel resting upon a dry 250-ml. volumetric flask, and washed quantitatively into the flask by means of absolute ethanol. As choline chloride is hygroscopic, it must be exposed as little as possible during the transfer. The solution is made up to below the mark, brought to room temperature, and finally made up to the mark. Aliquots are taken only when the solution is at its original temperature, in order to avoid errors caused by the high coefficient of expansion of alcohol. For choline citrate, a 9-gram sample is washed quantitatively into the volumetric flask by means of about 200 ml. of absolute ethanol to which about 4 ml. of concentrated hydrochloric acid has been added. After the contents of the flask are mixed a few times, more of the concentrated hydrochloric acid is added, a few drops at a time until all the sample is dissolved, and too great

an excess is avoided (about 1 ml. of concentrated hydrochloric acid in excess is used). The solution is then made up to volume with absolute ethanol. From this point on, the analysis of the chloride and of the citrate is the same.

PROCEDURE

Aliquots (25-ml.) are measured by means of a transfer pipet into 250-ml. wide-mouthed flasks, and 0.5 ml. of concentrated hydrochloric acid is added. With a minimum of delay in order to avoid absorption of moisture, a saturated solution of anhydrous cadmium chloride in absolute ethanol is added dropwise from a buret, rapidly but not as a stream, and with mechanical stirring. About 80 ml. are added, or an excess of 20 to 25 ml. above the volume equivalent to 0.45 gram of choline chloride or 0.90 gram of choline citrate. About 125 ml. of cadmium chloride solution were found to be approximately equivalent to 1 gram of choline chloride or 2 grams of choline citrate. After addition of the cadmium chloride solution, the stirrer is disconnected but is kept in the flask with the precipitated compound. The flask is placed overnight in the refrigerator, protected from moisture by a stopper bored to contain the stirrer, in order to obtain a quantitative precipitation for crude samples. Purified choline chloride samples can be analyzed merely by allowing the stoppered flasks to stand in an ice bath for about 1.5 hours. Complete precipitation of these samples is thus obtained.

The precipitated complex is transferred quantitatively while cold to a tared Gooch crucible containing an asbestos mat. Small portions of the saturated solution of the complex are used for transferring and for washing the material in the Gooch crucible. Three washings of the material in the crucible are made from a wash bottle with an exceedingly fine tip to remove the excess cadmium chloride. About 25 ml. of the wash solution are used altogether. The Gooch crucible is dried in the oven at 110°C . for at least 0.5 hour, after excess wash solution has been removed by suction, then cooled in a desiccator, and weighed.

Calculations. Grams of choline chloride =	
grams of precipitate \times	$\frac{139.63}{322.95}$
Grams of choline citrate =	
grams of precipitate \times	$\frac{295.29}{322.95}$

Table I. Solubility of Metallic Complexes of Choline Chloride

Salt Used	Approximate Solubility G./100 ml.
Mercuric chloride	0.4
Cobaltic chloride	0.1
Cupric chloride	0.1
Cadmium chloride	0.01

EXPERIMENTAL

Precision and Accuracy. A number of replicate values were obtained by the method on a sample of recrystallized choline chloride: 99.28, 99.22, 99.24, 99.14, 99.17, and 99.12; average 99.20%. The same sample had a moisture content, as indicated by the Karl Fischer method, of 0.68 and 0.70; average 0.69%. The standard deviation calculated from the replicate values is $\pm 0.06\%$ choline chloride. The total accounted for is 99.89%. The method would seem to have no constant error or, at most, about -0.1% .

Choline citrate, purified by recrystallization from a mixture of ethanol and methanol, gave duplicate values of 100.0% by precipitation of the cadmium chloride complex for 1.5 hours in an ice bath; and 99.7 and 99.6% after the complex was allowed to precipitate overnight in a refrigerator.

Choice of Cadmium Chloride as Precipitant. Of the metallic chlorides which were tried, ferrous chloride, lithium chloride, and nickel chloride showed no precipitation of choline chloride in absolute alcoholic solution. Table I gives some approximate solubility figures for the complexes formed with several other metallic chlorides. (The approximate solubility was determined

Table II. Effect of Water in Solutions Other Than Cadmium Chloride Solution

Solution	Total Water Present G./100 ml.	Error %
1	0.30	-0.04 ^a
2	0.73	-0.09
3	1.48	-0.17
4	2.93	-0.23
5	7.00	-0.46

^a Calculated from difference in errors for solutions 2 and 3. The value, 0.30 grams of water per 100 ml., is that of absolute ethanol and choline chloride without added water.

Table III. Effect of Water in Cadmium Chloride Solution

Water Added % by vol.	Weight of Precipitate Grams
2	1.0324, 1.0340
4	1.0700, 1.0371
4	1.6593, 1.4626

by evaporating to dryness in tared beakers 25-ml. portions of solutions of the respective metallic chloride complexes in absolute ethanol which had been saturated at room temperature.) The values given are expressed as equivalent grams of choline chloride per 100 ml. of solution in order to make a direct comparison possible.

Effect of Water. The presence of water in the sample or the reagents has two diverse effects upon the accuracy of the choline values. When the sample solution has water in addition to the normal low water content of absolute ethanol, but the saturated cadmium chloride solution has been made with absolute ethanol, low choline values are obtained (Table II). Column 2 gives the total water content of the ethanol solution of the sample and column 3 the error in terms of lowered percentages of choline chloride. The error, 0.04% for solution 1, agrees with that given in Table V, which corresponds to the normal method of analysis and was obtained by an entirely different procedure.

When, however, water was added not only to the aliquots of the sample solution and to the ethanol used in preparing the transfer and wash solution, but also to the ethanol with which the saturated cadmium chloride solution was made, values were obtained, as shown in Table III, which were both high and erratic. It is conceivable that the considerably higher concentration of cadmium chloride obtained by saturating aqueous ethanol rather than anhydrous ethanol may result in coprecipitation of cadmium chloride to an extent more than sufficient to offset the lower values caused by the presence of water in the other solutions.

Table IV. Effect of Excess of Cadmium Chloride

Saturated Cadmium Chloride Solution		Cadmium Chloride Complex Precipitated Grams	Choline Chloride Equivalent to Cadmium Chloride Complex Grams
Total Ml.	Excess Ml.		
60	5	1.0130	0.438
75	20	1.0158	0.439
90	35	1.0162	0.439

Determination of Suitable Excess of Cadmium Chloride. In order to determine what would be a suitable excess of cadmium chloride, the volume of cadmium chloride solution saturated at room temperature (26° C.) was first determined which would be approximately equivalent to a definite weight of choline chloride. This was done by running two analyses with measured volumes of cadmium chloride solution and slight excesses of choline chloride. The precipitated choline was calculated from the weights of complex obtained, and the ratio of the volume of

cadmium chloride solution to the choline chloride was calculated. Using this ratio as a basis for calculation, comparative analyses were made on equal portions of a volumetric solution of choline chloride, using 5, 20, and 35 ml., of cadmium chloride solutions, respectively, in excess of the calculated volume.

The figures in Table IV indicate that an excess of about 20 ml. of cadmium chloride solution saturated at room temperature would be suitable. Because the solubility of cadmium chloride was found to change from about 0.9 gram per 100 ml. of absolute ethanol at 10° C. to about 1.1 grams at 26° C., the reagent should be prepared at a temperature reasonably close to 26° C.

Solubility of Cadmium Chloride Complex. The approximate solubility of the cadmium chloride complex in absolute ethanol was determined by evaporating portions of solutions saturated at 28° and 0.5° C., respectively, in tared beakers. The effect upon the solubility caused by adding excess cadmium chloride was also determined by adding 10 and 20 ml., respectively, of cadmium chloride solution saturated at 26° C. to 80 ml. of the saturated solutions of the cadmium chloride complex and allowing the mixtures to stand overnight at the approximate temperature of saturation. The precipitates formed were then transferred quantitatively to tared Gooch crucibles and determined in the same manner as in an actual analysis. The difference between the solubility without excess cadmium chloride and the weight of solids thrown out by addition of the excess reagent indicates the solubility in the presence of the excess of reagent. The errors in the determination which could be due to the solubility of the complex would, therefore, be of the magnitude indicated by the values in Table V.

Table V. Effect of Excess Cadmium Chloride and Temperature on Solubility Errors

Excess Cadmium Chloride Solution Added Ml.	Temperature of Saturation ° C.	Solubility of Cadmium Chloride Complex ^a	
		Mg.	%
0	28	24.7	2.5
10	28	12.3	1.2
20	28	4.3	0.4
0	0.5	12.1	1.2
10	0.5	2.5	0.25
20	0.5	0.4	0.04

^a Assuming total weight of 1 gram of complex.

Table V indicates that the solubility errors can be made low by working at the lower temperature and using an excess of 20 ml. of cadmium chloride. The conditions described in the actual procedure are based upon these data.

Method of Precipitation. When the cadmium chloride solution was added by pouring from a graduated cylinder, and the solution was stirred by hand, high and erratic values were obtained. When the choline chloride solution was added to the cadmium solution (thus reversing the order of addition), high values were also obtained. When the two solutions were added dropwise from burets into absolute ethanol, with mechanical stirring so as to avoid an excess of either choline or cadmium chloride during the precipitation, more accurate and reproducible values were obtained. The method actually adopted was selected because it gave the same values as this procedure, but is more convenient. High values were also obtained when the cadmium chloride was added as a stream from a buret in about 5 to 10 minutes. A slow dropwise addition requiring about 40 minutes gave the same values as the 15- to 20-minute period recommended.

Time of Standing before Filtration. Recrystallized choline chloride was determined comparatively by the method described and by a modification whereby the mixture was cooled for only 1.5 hours by merely immersing in an ice bath. The values agreed, showing complete precipitation in the shorter period of time. The analysis of crude samples, however, gave lower values (usu-

ally by about 1%) in the shorter period of time. This would seem to indicate a slower precipitation of the less pure material.

Drying Time. Mere application of vacuum for 20 minutes did not dry the cadmium complex completely. Comparative drying of similar samples at 110° showed that 15 minutes were not sufficient for complete drying, while 30 and 60 minutes' heating gave identical values. This indicated that the drying is completed in 30 minutes.

Effect of Hydrochloric Acid. The presence of some free hydrochloric acid before the precipitation seems to be necessary for crude samples. A sample which gave values of 97.7, 98.4, and 98.2% (average 98.1%) of choline chloride in the absence of free hydrochloric acid gave 95.6, 95.7, and 95.8% (average 95.7%) when the analysis was conducted in the presence of free hydrochloric acid. Evidently lower and more reproducible values may be obtained in the presence of free hydrochloric acid. Yet in the case of purified choline chloride, the values obtained were unaffected by the presence or absence of free hydrochloric acid. This indicates that the acid did not interfere with the quantitative recovery of the cadmium chloride complex itself. A microscopic examination of the precipitates indicated that in the absence of free hydrochloric acid the compound precipitated in a poorer form. There were present several aggregates of very small crystals, or practically amorphous material, which could conceivably be accompanied by a coprecipitate of excess cadmium chloride; whereas the crystals obtained in the presence of the hydrochloric acid were large and well defined. The presence of the hydrochloric acid might prevent a possible coprecipitation of cadmium hydroxide by any basic impurity which might be present.

Composition of Cadmium Chloride Complex. Nitrogen was determined by a micro-Dumas procedure in the complex obtained by the use of a recrystallized choline chloride. The value found

was 4.34%; calculated for $C_5H_{14}NOCdCl_2$, 4.34%. In applying the method to unknown samples it may be well to determine the nitrogen content of the complex—for example, a sample of choline chloride mother liquor gave a complex which had a nitrogen value of 4.34 and 4.37%, whereas another sample of a different mother liquor gave nitrogen values of 3.56 and 3.57%. Evidently the second sample produced a precipitate contaminated with some impurity of low nitrogen content. The first sample gave crystals similar to those obtained with recrystallized choline chloride, whereas the second sample showed a mixture of these crystals with atypical forms.

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Determination of Tryptophan and Lysine in Microvolumes of Protein Hydrolyzates

Microbiological Method

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A procedure for the microbiological determination of tryptophan and lysine using microvolumes of protein hydrolyzate and small amounts of basal media is reported. Values obtained in assays on common proteins and on the proteins in chicken meat assayed by conventional methods have shown the method to be reliable and accurate.

IN THE microbiological determination of amino acids, particularly when only small quantities of sample material are available, any procedure that would reduce the amount of sample required would be desirable. Similarly, a procedure which would reduce the amount of medium required would result in an appreciable saving.

McMahan and Snell (5) reported a method for the microbiological determination of valine and arginine using a specially enriched medium in which a total volume of 2.5 ml. of hydrolyzate and medium was used for individual cultures. Hac *et al.* (3)

employed this method for determinations of glutamine and glutamic acid, and likewise reported satisfactory results. In a paper published since the completion of the present study, Henderson, Brickson, and Snell (4) described a micromethod for determination of amino acids which required total amounts of 2.0 ml. of combined sample and medium. Special microdispensers were used to facilitate operations, and electrometric methods were employed for titration of acid produced.

This paper describes a procedure for determination of tryptophan and lysine in protein hydrolyzates in which conventional media are used, but which requires total volumes of only 2 ml. of combined hydrolyzate and medium for each assay tube.

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Table I. L-Tryptophan and L-Lysine Content of Samples of Crude Fibrin and Lactalbumin Determined at Different Levels of Assay

Amount of Hydrolyzate per Assay Tube Ml.	L-Tryptophane Assay				L-Lysine Assay		
	0.05 N NaOH required		L-Tryptophan		0.01 N NaOH required		L-Lysine
	Ml.	γ	Per tube	In sample %	Ml.	γ	In sample %
Fibrin							
0.2	1.90	0.65	3.25	3.25	4.00	10.00	
0.2	1.90	0.65	3.25	3.40	4.20	10.50	
0.4	3.20	1.30	3.25	5.60	7.80	9.75	
0.4	3.20	1.30	3.25	5.40	7.60	9.50	
0.6	4.40	1.95	3.25	7.50	11.00	9.15	
0.6	4.40	1.95	3.25	7.50	11.00	9.15	
Av.			3.25 ± 0.0			9.67 ± 0.43	
Lactalbumin							
0.2	0.90	0.15	0.75	3.00	3.60	9.00	
0.2	0.70	0.10	0.50	3.20	3.80	9.50	
0.4	1.30	0.30	0.75	5.00	6.80	8.50	
0.4	1.30	0.30	0.75	5.10	7.00	8.80	
0.6	1.80	0.45	0.75	7.20	10.60	8.85	
0.6	1.80	0.45	0.75	7.30	10.80	9.00	
Av.			0.75 ± 0.0			8.94 ± 0.30	

The reliability of the method has been checked by simultaneous determinations using conventional methods on various protein hydrolyzates, and in all instances close agreement between values has been obtained. All equipment is readily available in the laboratory, and the procedure has been found of considerable practical value in routine determinations of the amino acids.

METHODS

Preparation of Inocula. *Lactobacillus arabinosus* 17-5 was used for the estimation of tryptophan and *Leuconostoc mesenteroides* P-60 for the determination of lysine, because these organisms give consistently good results when employed in conventional procedures. Inocula were prepared from stab stock cultures according to the method described by Schweigert *et al.* (7) and Dunn *et al.* (1).

Basal Media. Basal media were essentially those reported by Schweigert *et al.* (7) and Dunn *et al.* (1) and later modified by Reisen *et al.* (6). Tryptophan and lysine were omitted from the respective media in conducting the assays. The amino acids were dissolved in a minimum amount of 2 N hydrochloric acid, the mixture was diluted with a convenient volume of distilled water, and appropriate amounts of each of the other constituents were then added. After adjustment of the pH to 6.8 to 6.9, the completed media were diluted to proper volume.

Tryptophan and Lysine Standards. Standard solutions of tryptophan were prepared by dissolving 50 mg. of L-tryptophan (Merck) in 100 ml. of distilled water. Aliquots of 2.5 ml. of this solution made up to a volume of 250 ml. provided a solution with a concentration of 5 micrograms of L-tryptophan per milliliter.

Standard solutions of lysine were prepared by dissolving 50 mg. L-lysine hydrochloride in 100 ml. of distilled water. Aliquots of 10 ml. of this solution diluted to 250 ml. provided a solution containing 20 micrograms of L-lysine hydrochloride per milliliter.

Preparation of Samples. Samples for the determination of lysine were hydrolyzed by autoclaving with 2 N hydrochloric acid for 6 hours at a temperature of 121° C. For determinations of tryptophan, samples were hydrolyzed according to the enzymatic procedure described by Greenhut *et al.* (2) with pancreatin and hot mucosa. One-gram samples of fresh tissue, or 100- to 200-mg. samples of protein material, were used for each sample. Suitable dilutions were made to bring samples within the ranges of the assay curves.

Assay Procedure. Assay series were set up using 15 × 125 mm. Pyrex bacteriological test tubes. Serological pipets of 1-ml. capacity graduated to 0.01 ml. were used for additions of hydrolyzate and distilled water, and 5-ml. serological pipets graduated to 0.1-ml. divisions were used for addition of media.

For the standard curves, aliquots of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1.0 ml. of standard amino acid solution were used, and distilled water was added in amount sufficient to provide a volume of 1 ml. in each tube. Triplicate tubes were employed at the six lower levels to minimize the results of any anomalies which might occur, and duplicate tubes were used at the three higher levels. These aliquots of standard solutions provided curves ranging from 0 to 20 micrograms of L-lysine hydrochloride, and from 0 to 5 micrograms of L-tryptophan. Levels of 0.2, 0.4, and 0.6 ml. of hydrolyzate were used for each sample, duplicate tubes being

made at each level. As in the standard curve, water was then added to each tube to make a total volume of 1 ml. for the sample portion. Medium in the amount of 1 ml. was added to each tube, following which the tubes were plugged and autoclaved for 10 to 15 minutes at 121° C. After sterilization, the tubes were inoculated with one drop of the microorganism cell suspension from a special micropipet so constructed as to deliver 0.02 ml. per drop, and incubated as usual at 37° C. for 72 hours. The pipet was made from glass tubing of 2.5-mm. outside diameter drawn to capillary size at one end. This end was cut down until the orifice was of such diameter as to deliver exactly 50 drops per milliliter of contents.

Response of the microorganisms was measured by titration of the acid produced, using 0.01 N sodium hydroxide in the determination of lysine, and 0.05 N sodium hydroxide in the determination of tryptophan. Originally 0.01 N alkali was tried for both determinations, but acid produced by *Lactobacillus arabinosus* in the assay for tryptophan was found to be of such quantity as to merit the use of the stronger alkali. Titrations were carried out in the original tubes using a 10-ml. microburet graduated to 0.01 ml. The buret was fitted with a specially prepared delivery tip consisting of a glass tube drawn to capillary fineness at one end, and long enough to reach the bottom of the tubes. Simultaneously with the dropping of the alkali, air was allowed to bubble from the bottom of the tube through a similar glass capillary connected to an air pressure pump. The entrance of the air was regulated at a rate just sufficient to mix the contents of the tube thoroughly with the alkali. With this technique the precision of the titration was found to be increased, as the end point of the titration was sharply evident.

Table II. Recovery of Tryptophan and Lysine from Protein Hydrolyzates

Tryptophan			Lysine		
Present	Recovered	Recovery	Present	Recovered	Recovery
γ	γ	%	Mg.	Mg.	%
750	750	100	2.12	1.95	92.0
800	850	106	2.35	2.45	104.0
590	625	106	2.20	2.10	95.5
530	550	103	2.20	2.05	93.0

Table III. Tryptophan and Lysine Content of Chicken Meat Protein Determined in Macro and Micro Samples

Sample	Tryptophan		Lysine	
	Macro	Micro	Macro	Micro
	%	%	%	%
Fresh light meat	1.20	1.20
Fresh dark meat	0.92	0.82
Cooked light meat	0.71	0.68	8.14	7.75
Cooked dark meat	0.68	0.68	7.74	8.06
Canned light meat	0.55	0.42	7.96	8.42
Canned dark meat	0.57	0.53	7.15	8.62
Canned light meat	0.65	0.64
Canned dark meat	0.76	0.62
Cooked livers	1.01	0.93	6.76	7.06
Smoked meat	0.66	0.66
Cooked gizzards	6.80	7.07

RESULTS

Standard curves for lysine and tryptophan were typical of those obtained with conventional procedures. All curves obtained in repeated assays were similar, and showed consistent reproducibility.

Values for different levels of sample read from different portions of the curves for both lysine and tryptophan are given in Table I. Correlations between the different levels show that the curves obtained are reliable. Greatest arithmetical deviation from the average of these values was 4.5%.

Recovery values of both lysine and tryptophan are given in Table II. The values ranged from 100 to 106% with an average of 104% for tryptophan, and from 92 to 104% with an average of 96% for lysine.

Table III gives a comparison of values found for tryptophan and lysine in samples of chicken meat by both the regular assay methods and the method here discussed. These data reveal comparable values by both methods and demonstrate the reliability of the method.

DISCUSSION

The results obtained, clearly indicate the practicability of such a method for the determination of lysine and tryptophan. They further suggest that the method may be successfully used for the determination of other amino acids for which the microorganisms investigated show good response in conventional assay procedures.

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Gravimetric Calibration of Micrometers

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One of the main sources of error in scientific work is undoubtedly connected with calibration of weights and measures. The best means of obviating these is to obtain values by means of the instruments employed, using widely differing methods of procedure. Under these circumstances, agreement in checks constitutes almost certainty of the correctness of results obtained. An eyepiece micrometer was calibrated by comparing it with a stage micrometer evaluated by the manufacturer or other agency.

OCULAR micrometers are ordinarily calibrated by means of previously standardized stage micrometers. The details of this procedure can be found in practically all texts on chemical microscopy, such as that of Chamot and Mason (2). An entirely different and independent method of calibrating eyepiece micrometers by a gravimetric method is desirable both for its own sake and as a check on the classical method of calibration. Results obtained in the chemical laboratories of the University of Oklahoma show that the gravimetric method of accomplishing this objective is entirely feasible and satisfactory. Briefly, this method consists in weighing a substantially perfect sphere of a pure noble metal, as the gold used in this study, on a sensitive microbalance.

The volume of the gold spherical bead is then calculated from its known weight and density. From the volume, the diameter is calculated and applied as a primary standard to the unknown scale of the ocular micrometer undergoing calibration.

APPARATUS

The apparatus employed consisted of a gold assay balance rated at a sensitivity of 0.002 mg. The stage micrometer used in checking the results of the gravimetric calibration was divided into 0.01- and 0.10-mm. intervals. All measurements were made in accordance with established methods of procedure (2, 3). Pertinent representative data are summarized in Table I.

SPECIAL PROCEDURES

The spheres of gold were formed on ordinary wood charcoal blocks before the common mouth blowpipe ordinarily employed in blowpipe analysis. The "synthetic" charcoal blocks currently on the market proved unsatisfactory because of a fusible ash or flux formed on the metallic beads when such blocks were employed. These synthetic blocks appear to have been made by pressing charcoal fragments together in some sort of a binder. The wood charcoal blocks formed a substantially infusible ash that was blown away instead of adhering to the bead. No difficulty was experienced in connection with perfect sphericity of the beads, as representative data in Table II make clear. The measurements given were taken in all possible orientations. They were facilitated by use of the rotating stage of the microscope for directions in a horizontal plane and the beads were turned over manually for different orientations in other directions.

The apparatus was also calibrated directly by means of a spherical pure gold bead, the diameter of which was calculated from its weight obtained on a sensitive microbalance and its known density. This diameter applied to the unknown scale of the eyepiece micrometer as a primary standard of length serves to calibrate the instrument. Concordant values obtained by the two different methods serve as conclusive evidence of validity of gravimetric calibration of the scale in the eyepiece micrometer.

DISCUSSION

Although satisfactory results have been obtained with pure gold beads and almost as good agreement has been experienced in connection with pure silver, the reverse is true with beads of gold-silver alloys submitted to the same treatment. The results are so far from satisfactory that no instance can be cited where theoretical percentages could be calculated from weight-volume

Table I. Gold Beads

No. of Bead	Weight of Bead, Mg.	Volume of Bead ^a , Cc.	Calculated Diameter of Bead, Cm.	Av. Micrometer Divisions Subtended by Diameter ^b
1	3.30	1.71×10^{-4}	0.0688	44.4
2	3.08	1.60×10^{-4}	0.0674	43.1
3	2.37	1.23×10^{-4}	0.0616	38.9
4	3.00	1.56×10^{-4}	0.0668	42.7

^a Optical system of 7.5 × eyepiece, 10.0 × objective, and 160-mm. tube length. Weight/19.32.

^b Summarized representative results from Table II.

Table II. Sphericity Tests on Gold Beads of Table I

(Small divisions of micrometer subtended by different diameters of gold beads^a)

Gold Bead 1, Diameter 0.0688 Cm., Divisions	Gold Bead 2, Diameter 0.0674 Cm., Divisions	Gold Bead 3, Diameter 0.0616 Cm., Divisions	Gold Bead 4, Diameter 0.0668 Cm., Divisions
44.3	43.5	39.6	42.4
44.3	43.1	38.1	42.5
44.6	43.1	39.7	42.5
44.4	43.0	39.1	42.8
44.4	42.8	39.0	42.6
44.4	43.1	38.5	42.8
44.3	43.1	39.5	43.0
44.4	43.0	38.6	42.9
44.5	43.2	38.8	43.0
44.3	43.0	38.3	42.9
44.4	43.1	38.9	42.7
Av. 44.4	43.1	38.9	42.7
Diameter/division 0.0688/44.4	0.0674/43.1	0.0616/38.9	0.0668/42.7
1 division, cm.	0.00155	0.00156	0.00159

Av. 0.00156 cm. (mean value)
Accepted value by calibration with stage micrometer, 0.00157 cm. (mean value)

^a Optical system of 7.5 × eyepiece, 10.0 × objective, and 160-mm. tube length.

relationships by the application of the law of mixtures. This is particularly disappointing, for such a procedure would enable an assayer to arrive at the percentage composition of gold-silver alloy beads without the operations of inquartation, parting, and annealing, which are much more time-consuming and involve a greater risk of loss than would the type of determination under examination. However, theoretically, an empirical curve relating true composition to values experimentally determined, even though they are not stoichiometric, should enable the objective to be realized. Such a curve has been constructed in these laboratories and this phase will be reported on later.

Chamot and Mason (3) state that "if the substance can be made to take the form of a sphere, the results may be highly accurate." Blank and Willard (1), citing the same authorities (4-6), state flatly that microdensity determinations, which depend upon the same data, cannot be made accurately by these methods. Evidence obtained in these laboratories shows that results are stoichiometric in the case of pure noble metals but it has not been possible, so far, to obtain comparable results with

gold-silver alloys. This paper attempts to prove that observed discrepancies are not connected with weight determination or errors in mensuration.

ACKNOWLEDGMENTS

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NOTES ON ANALYTICAL PROCEDURES

Spectrographic Determination of Phosphorus and Metals in Lubricating Oils, Using a Porous Cup Electrode

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IN spectrographic methods for the rapid analysis of lubricating oils for phosphorus and metal additives, one of the chief difficulties has been that of introducing the sample into the arc or spark. Methods in which the sample is ashed usually give erratic results, whereas those which involve electrodes impregnated with the oil sample have been more successful.

In a method described by Calkins and White (1), impregnated electrodes were prepared by heating graphite rods to white heat and quenching them in the oil to be analyzed. When attempts were made to use a similar procedure in these research laboratories although satisfactory results were obtained for the same base oil, different analytical curves for phosphorus were required for different base oils. These differences have been minimized in the method described below.

EQUIPMENT

The equipment used included a 2-meter grating spectrograph, Multisource excitation unit, and densitometer manufactured by the Applied Research Laboratories.

METHOD

A sample of the oil to be analyzed is placed in a porous cup electrode (2) formed from National Carbon Company special graphite spectroscopic electrodes 6.35-mm. in diameter. The cup is made by drilling a cavity 3.96 mm. in diameter in a rod 22.23 mm. long, leaving a bottom thickness of 0.635 mm. through which the sample seeps. The cup is used as the upper electrode; a rod 6.35 mm. in diameter with a 45° included angle cone tip is used as the lower electrode. The spark gap is 3.175 mm.

The excitation is provided by setting the Multisource unit at 5-microfarad capacitance, 25-microhenry inductance, and 0.4 ohm-resistance. The charge vs. discharge switch is set at 180°. A 30-second prespark time is followed by a 60-second exposure. The grating aperture is set at 0.7 of the maximum. A 50-micron slit width is used. The spectra are recorded on Spectrum Analysis No. 2 film. These conditions give a film background of approximately 50% transmittance.

The film is developed for 3 minutes in D-19 developer at 20° C., hardened for 15 seconds in potassium chrome alum hardener, and fixed for 6 minutes in Kodak acid fix.

The transmittances of the phosphorus line at 2535.65 Å. and of the film background immediately adjacent to it are measured with the densitometer. The film background is used as internal standard as described by Calkins and White (1), but the element line is corrected for film background. Film calibration is made from iron spectra photographed through a two-step filter.

DISCUSSION

A method of analysis using electrodes quenched in the oil sample was found unsatisfactory.

Electrodes were impregnated with the oil sample by heating graphite rods to 1000° C. in a muffle furnace and quenching them in the oil to be analyzed. The oil-impregnated graphite rods were used for both the upper and the lower electrodes and were excited by an overdamped spark discharge (Multisource, 30-microfarad capacitance, 150-microhenry inductance, and 18-ohm resistance) which was found to minimize variations that occurred when different additives were used as the source of phosphorus.

This method gave reproducible results, regardless of the type of additive present, as long as the same base oil was used. A change in the type of base oil caused a shift in the analytical curve.

It was thought that this behavior might be the result of partial decomposition of the sample on the introduction of the hot graphite electrode. A porous cup electrode similar to that used by Feldman (2) was then tried as a means of introducing the oil into the spark at room temperature; the oil sample was contained in the cup as the upper electrode and allowed to seep through the thin bottom. A cone-tipped graphite rod was used as the counter-electrode. A cup with a bottom wall thickness of 1.0 mm. eliminated the shift of the analytical curve that occurred with different oils but gave occasional erratic exposures, which were eliminated by reducing the thickness of the bottom wall to 0.635 mm. A sample of approximately 1 ml. was sufficient for duplicate determinations with the porous cup as compared to approximately 20 ml. required for quenching electrodes in the oil. The use of the porous cup electrode required more sparklike excita-

Table I. Comparison of Results with Quenched and Porous Cup Electrodes

(Results: weight %)

Base Oil	Additive	Phosphorus Added	Phosphorus Found	
			Quenched electrodes	Porous cup electrodes
A	Calcium, zinc, phosphorus additive	0.100	0.100	0.098
A	Triphenylphosphine	0.100	0.105	0.097
A	Barium, phosphorus additive	0.100	0.105	0.102
A	Tri- <i>o</i> -cresyl phosphate	0.100	0.105	0.105
B	Barium, phosphorus additive	0.100	0.086	0.101
C	Triphenylphosphine	0.094	0.076	0.092
D	Barium, calcium, zinc, phosphorus additive	0.198	0.100	0.200
D	Barium, calcium, zinc, phosphorus additive	0.021	0.010	0.020
E	Tri- <i>o</i> -cresyl phosphate	0.150	0.112	0.147
E	Tri- <i>o</i> -cresyl phosphate	0.050	0.043	0.055

Table II. Effect of Viscosity on Phosphorus Determination

(Results: weight %)

Viscosity	Phosphorus Added	Phosphorus Found
SAE 10	0.150	0.147
	0.050	0.055
SAE 20	0.101	0.102
	0.050	0.050
SAE 40	0.150	0.136
	0.050	0.048

tion (Multisource, 5-microfarad capacitance, residual inductance and resistance). Intensity ratios obtained with this discharge became constant after 30 seconds and remained so for several minutes of continued sparking. A 60-second exposure was used to give the desired line intensities. Only a small portion of the sample contained in the cup (approximately 0.35-ml. total volume) was consumed during the sparking period.

The shape of the counterelectrode had little effect on the intensity ratios obtained. Counterelectrodes with hemispherical tips and electrodes tipped with cones of 10°, 45°, 90°, and 120° included angles gave almost identical intensity ratios. The 45° cone was selected for its slightly greater reproducibility.

Spark gaps of both 1.59 and 3.18 mm. were tried. Intensity ratios of the same magnitude were obtained with each, but the wider gap gave somewhat better reproducibility.

The use of the continuous film background as internal standard (1) was found satisfactory, provided the line intensity was corrected for background. The use of nickel as an added internal standard had no advantages over film background.

The effect of base oil and the nature of the phosphorus additive were studied by analyzing known samples of five different base oils. Four of these oils had given markedly different intensity ratios for the same phosphorus concentration by the quenched electrode method. The use of the porous cup electrode gave intensity ratios which permitted the use of the same analytical curve for all five base oils (Table I).

In the course of the investigation, five different additives were used as the source of phosphorus in the samples. The nature of the additive apparently had no effect on the phosphorus determination (Table I).

The effect of viscosity was investigated by analyzing known samples ranging in viscosity from SAE 10 to SAE 40. Within these limits, changes in viscosity had no significant effect on the phosphorus determination (Table II).

The accuracy of the method was calculated from 90 determinations made on samples which included the five types of base oil and the five phosphorus additives mentioned above. The concentration range covered was 0.05 to 0.20% phosphorus. The average per cent deviation from the known value was 5.4%; the standard deviation, expressed as per cent of phosphorus present, was 6.8%. The largest single error in the 90 determinations was 16%. Somewhat larger deviations occurred below 0.05% concentrations, an average per cent deviation of 12.5%

being obtained for the concentration range of 0.01 to 0.05%. The limit of detection was approximately 0.01% phosphorus.

The method is being extended to include determinations for barium, calcium, and zinc in concentration ranges from 0.01 to 0.20% for each metal. Satisfactory analytical curves have been constructed for these elements, but the influence of the type of base oil and the nature of the additive has not been investigated as fully as in the case of phosphorus. No difficulty has been encountered with the oils and additives used thus far. As in the case of phosphorus, film background was used as the internal standard and the element line was corrected for background intensity. The barium line at 2335.27 Å., the calcium line at 4302.53 Å., and the zinc line at 3345.02 Å., were used as analysis lines. It is planned to extend the method to include the analysis of both clarified and nonclarified used oils.

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Modified Silica Replica Technique

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THE preparation of silica replicas is a well established technique in electron microscopy.

The authors have been using a conical basket, made of 20-mil tungsten wire, as the heating element for vaporizing silica in high vacuum. If a pellet of quartz is placed in the basket, this source of silica makes a large number of replicas. However, a large current and relatively long periods of heating are necessary to vaporize quartz from a pellet effectively. Because the relatively large mass of quartz consumes a considerable amount of heat before reaching the sublimation temperature, the authors have preferred to use thin fibers of quartz laid in the basket so as to make good contact with the tungsten wire.

It has recently been found that a colloidal silica dispersion (Du Pont Ludox) is well suited for use in the preparation of silica replicas. Ludox may be used in two ways, both of which shorten the time of evaporation required to obtain a silica replica and eliminate the need for drawing out thin quartz rods as a source of silica.

In the first method flakes, which may be obtained by allowing some Ludox to evaporate in a beaker or on a glass slide, are packed in the tungsten basket. In the second method a clean tungsten filament (basket) is dipped four times in Ludox; time is allowed for the dipped filament to dry before each successive dipping. In this manner a film of the material is deposited on the tungsten wire itself. On a third tungsten filament are hung four or five quartz fibers prepared by heating and drawing out 0.6-cm. (0.25-inch) quartz rods hooked on one end. The average drawn fiber is approximately 0.5 mm. in diameter.

Positive silica replicas of polystyrene negative replicas of a microscope cover glass were prepared in a vacuum unit equipped with three pairs of heating elements, so that the three sublimations could be carried out in approximately the same vacuum, less than 0.1 micron. The same current, 25 amperes, was passed through each filament, and the relative lengths of time (seconds) required to obtain silica films of comparable thickness are: quartz fibers, 45; Ludox flakes, 15; filament dipped in Ludox, 10 or less.

The dipped filament gave only about three satisfactory silica films before it was necessary to recoat it. When Ludox was used,

a white residue was left on the tungsten filament after each evaporation. Silica films prepared by these three methods were compared in the electron microscope and found to be alike in all respects. There was no evidence of any abnormal amounts of foreign matter on replicas prepared from Ludox. The effectiveness of the evaporation of silica from Ludox is probably due to the very small particle size of the silica and its better contact with the tungsten wire.

The technique in which the tungsten filament is dipped in Ludox is undesirable because of the limited number of samples that can be prepared before coating the filament again. Because a large number of easily prepared flakes of Ludox may be placed in the basket, this method does not suffer from the same limitation.

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Continuous Purification of Water for Isotopic Analysis by Density Determinations

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FOR the isotopic analysis of water by density determination, an apparatus for the continuous or batch purification of small samples of water was needed. Purified water without significant change of isotopic composition and of a density correct to less than 1 p.p.m. was desired

The simplest form of the apparatus developed for this purpose is shown in Figure 1. It is of Pyrex. Water is allowed to flow

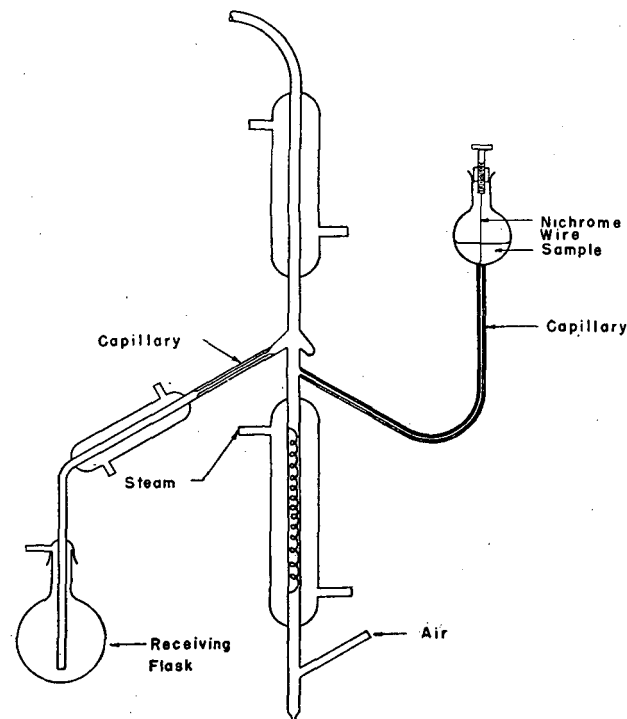


Figure 1. Diagram of Apparatus

down a steam-jacketed tube, up which a current of air is passed. The evaporator tube contains a closely fitting helix of 20 gage Nichrome wire to provide a longer path and better distribution of liquid flow. The rate of admission of water is controlled by the degree of penetration of a Nichrome wire into a capillary of but slightly greater diameter. Air or tank nitrogen is purified by passage over heated copper oxide at 600° C. and thence through long towers of soda-lime and calcium chloride. Some results indicated that such purification may be more than necessary, but elimination of grease and oil from the air is important. The relative rates of air and water flow are adjusted to keep liquid from the lower third of the evaporator tube. Evaporation takes place without boiling or spray formation. For a tube of 1-cm. internal diameter and 50 cm. long, a suitable rate is 1 ml. of water and 0.4 liter of air per minute.

Water is condensed in the condenser and flows down to the catch basin, whence it is diverted to the collector system. It is thus collected and removed from the system while hot (about 90° C.). Nonvolatile impurities remain in the evaporator. They may be discharged from the bottom of the column by shutting off the air flow for a few minutes daily. Most volatile impurities remain in the air stream. The purpose of the sections of capillary in the collector system and at the bottom is to retain slugs of water and prevent the gas feed from leaving by these routes.

The general performance of the unit is shown in Table I. The content of carbon dioxide is reduced to 1% of the initial in one evaporation, that of ammonia to 10% in one cycle or to 1% in two. Nonvolatile materials such as barium and calcium nitrates and ammonium phosphate are completely removed. A volatile material such as nitric acid which forms a maximum boiling azeotrope with water is not removed but accumulates in the evaporator and gradually appears in the distillate. The conventional use of barium hydroxide removes it.

The unit shown in Figure 1 is suitable for the purification of tap water or water containing only inorganic salts. Feed water containing dilute nitric acid should be passed through a tube containing pellets of lime inserted just before the evaporator. The output of this unit should then be fed into a second evaporator whose output is so collected that the condensate remains out of contact with air after it has been cooled. Very satisfactory continuous purification can be obtained.

A number of determinations of the densities of purified water were made by the float method and compared with those of the same samples purified by the technique of Dole and Slobod (1). The extreme deviation was 1.3 p.p.m., the average, 0.4 p.p.m.

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Table I. General Performance of Purification Unit

Solution Fed	Initial Specific Conductivity	Initial Concn. of Electrolyte, M	Final Conductivity	Final Concn. of Electrolyte, M
Laboratory distilled water	5×10^{-6}	0.02 ...	1×10^{-6}	0.0002
Solution of CO ₂	1.06×10^{-4}	0.01	3.5×10^{-5}	0.001
Solution of NH ₃	3.5×10^{-5}	0.001	1.0×10^{-5}	0.0001
0.001 M NH ₃ + excess H ₃ PO ₄	...	0.0003	0.75×10^{-5}	...
Ca(NO ₃) ₂	...	(NH ₃) ₂ PO ₄ + H ₃ PO ₄	1.1×10^{-6}	...
Dilute HNO ₃	6×10^{-5}	0.1	5.4×10^{-6a}	1.3×10^{-5a}
0.005 M HNO ₃ + excess Ba(OH) ₂	...	1.4×10^{-4}	0.8×10^{-6}	...
		0.0025		
		Ba(NO ₃) ₂ + Ba(OH) ₂		

^a Conductance fell initially to 0.8×10^{-6} ; then rose with successive fractions to value listed.

Voskuyl, who collaborated with the authors on other phases of the research, contributed by his counsel to the development of the equipment described in this paper.

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RECEIVED February 4, 1948.

Sensitization of Fuchsin-Sulfurous Acid Reagent for Formaldehyde by Addition of Ketones

CARROLL L. HOFFPAUIR AND ROBERT T. O'CONNOR

Southern Regional Research Laboratory, New Orleans, La.

FUCHSIN-sulfurous acid reagent for the qualitative or quantitative determination of small quantities of formaldehyde has been used for many years (1, 2, 3). Efforts to increase its sensitivity have usually been directed toward holding the sulfurous acid content to a minimum. Thus, Tobie (5) suggests reducing the sulfur dioxide content from 5 to 2 grams per liter, and points out (4) that the presence of considerable ethanol intensifies the color. The present authors have observed that the presence of acetone causes the development of a more intense color in the reaction of a given amount of formaldehyde and a given amount of fuchsin-sulfurous acid reagent.

In order to follow this effect, to known amounts of a standardized solution of formaldehyde in a 25-ml. volumetric flask were added 5 ml. of 12 *N* sulfuric acid, 10 ml. of fuchsin-sulfurous acid reagent (2), and increasing amounts of acetone. The flasks were made to volume with water, the reagents mixed, and the per cent transmittance was determined by means of an Evelyn photoelectric colorimeter with a No. 565 filter. The blanks for setting the instrument contained all reagents, but distilled water was used to replace the formaldehyde solution.

Increasing amounts of acetone up to 2 ml. increase the intensification of color, but further increases in amount of acetone produce no further intensification. As shown in Figure 1, in the presence of acetone 3.25 hours are required for maximum color development compared to 2 hours for maximum color development in the absence of acetone. The color developed is more stable in the presence of acetone. Spectrophotometric curves plotted in Figure 2 show that though the maximum color is more intense in the presence of acetone, there is no shift in the wave length of maximum absorption nor any change in the nature of the curve in the visible spectrum. The curve of per cent transmittance *vs.* concentration in the presence of acetone differs only

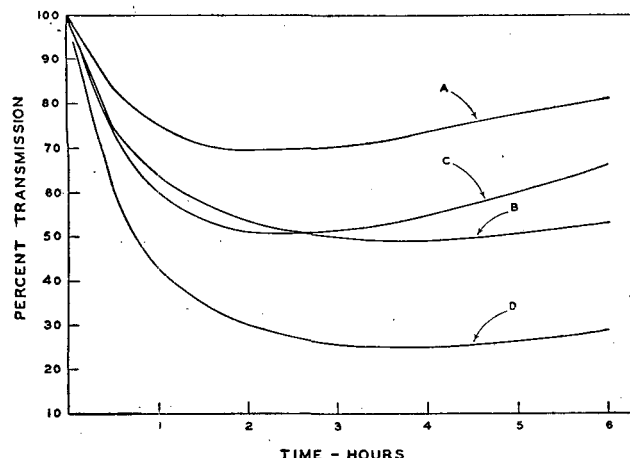


Figure 1. Transmittance vs. Time

Evelyn colorimeter, 565 filter

- A. 0.046 mg. CH_2O and 10 ml. fuchsin-sulfurous acid per 25 ml.
 B. 0.046 mg. CH_2O and 10 ml. fuchsin-sulfurous acid and 2 ml. acetone per 25 ml.
 C. 0.069 mg. CH_2O and 10 ml. fuchsin-sulfurous acid per 25 ml.
 D. 0.069 mg. CH_2O and 10 ml. fuchsin-sulfurous acid and 2 ml. acetone per 25 ml.

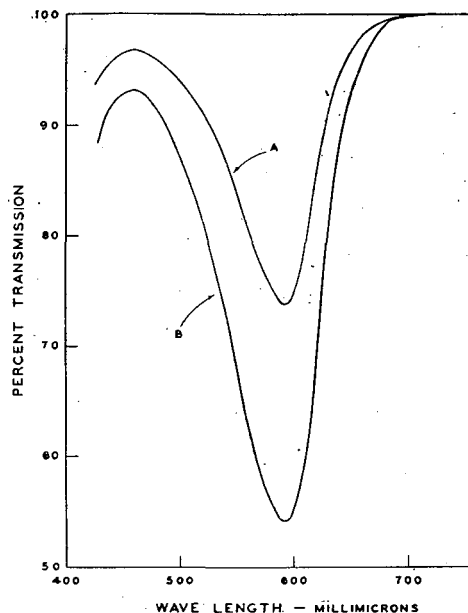


Figure 2. Transmittance Curves of Formaldehyde-Schiff's Reagent

- A. Schiff's-formaldehyde color
 B. Schiff's-formaldehyde color in presence of acetone

in intensity of absorption from that previously published in the absence of acetone (2).

Similar effects were noted for methyl *n*-propyl ketone, diethyl ketone, diacetone alcohol (4-hydroxy-4-methyl-2-pentanone), and methyl ethyl ketone. The time of maximum color development and intensity were essentially the same as in the presence of acetone. Ethylene glycol was found to intensify the color slightly. However, fructose, a ketose, had no effect on the time or intensity of the color developed by fuchsin-sulfurous acid reagent with formaldehyde. As none of these ketones produces any more intense color than acetone, the use of this common solvent is recommended where maximum sensitivity is required when the fuchsin-sulfurous acid reagent is used.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Elsie T. Field in obtaining the spectrophotometric data used in these studies.

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RECEIVED April 2, 1948.

CRYSTALLOGRAPHIC DATA

Contributed by Armour Research Foundation of Illinois Institute of Technology

16. Allylthiourea (Thiosinamine)

EXCELLENT crystals of allylthiourea are obtained from water either on a microscope slide (Figure 1) or on a larger scale. All the crystals used in this work were obtained in this way; large crystals for x-ray diffraction were crystallized slowly by evaporation of an aqueous solution.

Allylthiourea exists in at least two polymorphic forms. The stable form is most readily (and perhaps always) obtained by recrystallization from water. The unstable form is always ob-

tained during recrystallization from the melt at room temperature. Figure 1 shows the solution phase transformation at room temperature. The large well-formed rods of I are growing at the expense of the fine grained crystals of II in thymol.

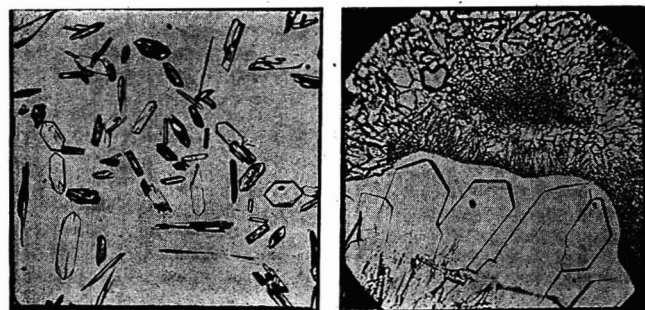


Figure 1. Allylthiourea

Left. Crystals from water on microscope slide
Right. Solution phase polymorphic transformation in thymol on microscope slide

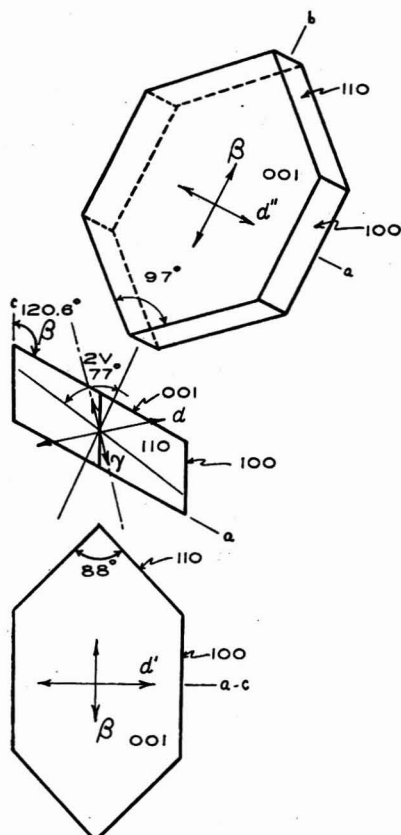


Figure 2. Orthographic Projection of Typical Crystal of Allylthiourea

ALLYLTHIOUREA (I)

CRYSTAL MORPHOLOGY (determined by W. C. McCrone).

Crystal System. Monoclinic.

Form and Habit. Tablets and rods elongated parallel to b , showing the basal and orthopinacoids $\{001\}$ and $\{100\}$; prisms $\{110\}$; clinodome $\{011\}$; and several other orthodome forms including $\{201\}$, $\{502\}$, $\{301\}$, and $\{401\}$.

Axial Ratio. $a:b:c = 1.14:1:0.976$.

Interfacial Angles (Polar). $110 \wedge 1\bar{1}0 = 88^\circ$; $011 \wedge 0\bar{1}1 = 79^\circ$.

Beta Angle. $120^\circ 36'$.

X-RAY DIFFRACTION DATA (determined by J. F. Whitney and I. Corvin).

Cell Dimensions. $a = 9.76 \text{ \AA}$; $b = 8.57 \text{ \AA}$; $c = 8.37 \text{ \AA}$.

Formula Weights per Cell. 4.

Formula Weight. 116.18.

Density. 1.249.

Principal Lines

d	I/I_1	d	I/I_1
7.32	0.49	2.37	0.08
5.76	0.32	2.34	Very weak
5.56	0.13	2.30	0.04
4.24	1.00	2.25	0.08
3.83	0.69	2.18	Very weak
3.70	0.40	2.15	Very weak
3.54	0.08	2.11	Very weak
3.37	Very weak	2.07	0.13
3.22	0.26	2.02	0.13
3.05	0.49	2.00	Very weak
3.00	0.31	1.94	0.06
2.93	0.11	1.90	0.09
2.78	0.09	1.87	0.05
2.66	0.11	1.81	Very weak
2.60	0.14	1.79	Very weak
2.53	0.08	1.77	Very weak
2.49	0.09	1.72	Very weak
2.42	Very weak	1.69	Very weak

OPTICAL PROPERTIES (determined by W. C. McCrone and A. Smedal).

Refractive Indexes (5893 \AA ; 25°C). $\alpha = 1.602 \pm 0.002$.
 $\beta = 1.684 \pm 0.002$. $\gamma = 1.74 \pm 0.01$.

Optic Axial Angles (5893 \AA ; 25°C). $2V = 77^\circ$. $2H = 88^\circ$.
Dispersion. $v > r$.

Optic Axial Plane. 010 .

Sign of Double Refraction. Negative.

Acute Bisectrix. $\gamma \wedge c = 15^\circ$ in acute β .

Extinction. $\alpha \wedge a = 45^\circ$ in obtuse β .

Molecular Refraction (R) (5893 \AA ; 25°C). $\sqrt[3]{\alpha\beta\gamma} = 1.67$
 R (calcd.) = 35.1. R (obsd.) = 34.8.

FUSION DATA (determined by W. C. McCrone).

Allylthiourea melts at $77-78^\circ \text{C}$ with neither decomposition nor sublimation. Crystallization is spontaneous and may give either fine grained crystals of the unstable form which grow rapidly or coarse grained rods of the stable form which grow slowly. The transformation occurs only very slowly even in the presence of thymol melt or water as a solution medium.

Allylthiourea (I) grows elongated parallel to b and shows all possible interference figures [$2V = 77^\circ$; $v > r$; (-)] and orientations. Allylthiourea (II) is very slowly changed to I at room temperature. A meltback of II gives larger rods which show $2E = 128^\circ$; $v > r$; (+).

CORRECTION. In the article on "Rapid Wet Combustion Method for Carbon Determination" by Lindenbaum, Schubert, and Armstrong [ANAL. CHEM., 20, 1120 (1948)], the reagent used in the authors' experiments was incorrectly named. The term chromium trioxide and the formula CrO_3 should have been used instead of chromic oxide and Cr_2O_3 .

SCIENTIFIC COMMUNICATIONS

A New Subtype of Olefin

THE recent announcement of the availability of trans-4-methyl-2-pentene as part of the A.P.I.-sponsored list of National Bureau of Standards standard samples of hydrocarbons will direct attention to the unusual properties of this compound and its corresponding cis-isomer (1). The infrared spectra and chemical properties of these compounds indicate that in this pair the normal boiling point order is somehow reversed, so that the lower boiling form (55.8° C.) is the cis-isomer and the higher boiling form (58.7° C.) trans. They are apparently the first members of a new subtype of olefin, which show a reversal of the boiling point relationship normally expected between cis and trans isomers.

This compound is a Type II olefin in the Boord system of classification (4), part of the homologous series derived from cis- and trans-2-butene. On the basis of Kistiakowsky's work establishing the structure of the two 2-butenes (2), it has usually been assumed that the cis-olefin in such a pair is the higher boiling isomer. Olefin type analysis by infrared spectroscopy (3) tends to confirm this assumption, as the "trans-II olefin peak" at 10.3 microns is common to the lower boiling isomers of 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, 3-heptene, and 2-octene, while the corresponding "cis-II olefin peak" at about 14.3 to 14.7 microns appears in the spectra of their higher boiling isomers.

In the case of the 4-methyl-2-pentenes, however, the higher boiling isomer has the characteristic peak at 10.3 microns which usually indicates a trans-II configuration, while the lower boiling isomer has its peak more nearly in the cis-II region at 13.9 microns. The lower boiling isomer is more reactive chemically, and less rather than more of it is found in the mixture obtained on synthesis. (Samples and chemical data were supplied by courtesy of N. C. Cook and the late F. C. Whitmore, Pennsylvania State College, State College, Pa.) These data all point to the conclusion that in this case the lower boiling isomer is cis rather than trans, and vice versa for the higher form.

A study of molecular models shows that there may be some interaction between the double bond and a "penadjacent" alkyl group on the carbon atom one atom removed therefrom. This is particularly true in the cis form of the molecule. On the other hand, where the alkyl groups are further down the chain as in the 5,5-dimethyl-2-hexenes, or where there are two alkyl substituents instead of one in the penadjacent position, as in the 4,4-dimethyl-2-pentenes, additional infrared data show that the normal order of boiling points appears.

In the case of the 2-methyl-3-hexenes the same penadjacent alkyl grouping appears as in the 4-methyl-2-pentenes, and the order of boiling points is again reversed so that the high-boiling isomer shows the trans-II peak in its infrared spectrum. The cis-II peak for the corresponding low-boiling isomer shows a still further shift toward a shorter wave length, appearing at 13.6 microns.

The fact that at least one higher olefin pair of related structure shows the same reversal of boiling points as the 4-methyl-2-pentenes suggests that olefins of this structure may be regarded as a subtype under the Type II classification. Because compounds of this type are recognizable by molecular structure as well as by infrared spectra, they may be separately labeled as "cis-II-p" and "trans-II-p" olefins. The "-p" refers to the penadjacent alkyl grouping —CHR:CH—, as a subtype of the Type II olefin —CH:CH—. The "trans-II-p" infrared absorption peak still appears at the normal trans-II wave length, while the

"cis-II-p" peak has been shifted to wave lengths shorter than the usual cis-II region. It is possible, therefore, that the trans forms of these olefins may be considered as having their normal boiling points, and the abnormally low boiling points of the cis isomers may be related to the restricted freedom of internal rotation within the molecule.

Additional examples of this subtype can be expected to occur among the olefins of higher molecular weight, so that a significant fraction of the total number of Type II olefin pairs may show this reversal of the normal order of boiling points. There is a possibility that "cis-II-p" olefins of this subtype can be identified as a group by virtue of the shift in wave length of the characteristic peak in their infrared spectra, which will be further investigated.

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HOMER J. HALL
IRENE A. MIKOS

Eso Laboratories, Research Division
Standard Oil Development Co.
Elizabeth, N. J.

Merck Graduate Fellowship in Analytical Chemistry

Merck & Co., Inc., Rahway, N. J., is sponsoring one fellowship for a year of graduate work in analytical chemistry to be available first in 1949. Renewal is permissible, but no fellow may hold this appointment for more than three years. The annual stipend is \$2500.

The fellowship will be awarded to that applicant who the Selection Committee believes will contribute most to the advancement of the theory and practice of analytical chemistry during the tenure of the fellowship and the course of his future career.

Application should be made on a special form which can be obtained from the AMERICAN CHEMICAL SOCIETY, 1155 Sixteenth Street, N. W., Washington 6, D. C. It must be accompanied by an outline of a proposed research and study program to be carried out in the United States or Canada under the direction of a person of established reputation in the field of analytical chemistry. In the United States, the fellow must enroll in an institution whose undergraduate course of instruction in chemistry is approved by the Society; in Canada, the institution selected must, in the opinion of the Chemical Institute of Canada and the AMERICAN CHEMICAL SOCIETY, provide facilities and instruction comparable with those of approved departments in the United States. A fellowship will be voted contingent upon the successful candidate's promptly obtaining acceptance from the institution and professor selected for the study program proposed.

Completed application forms, letters of recommendation, and transcripts of credits should be sent to the AMERICAN CHEMICAL SOCIETY, and must be received not later than May 1, 1949.

BOOK REVIEWS

Radioactive Indicators. Their Application in Biochemistry, Animal Physiology, and Pathology. *George Hevesy.* xvi + 556 pages + Segre isotope chart. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y., 1948. Price, \$10.

The stated purpose of this book is to survey the work carried out in the fields indicated by the title, and if all the reader requires is a survey, he will probably be satisfied. Its contents give a good idea of the way in which various investigators have tried to use radioactive isotopes to solve varied problems, and provide some conception of the information to be gained from experiments with tracers.

The first 95 pages are concerned with the production, usefulness, and determination of radioactive isotopes, together with a brief discussion of atomic interchange and the application of isotopes to analytical problems. The body of material appears in six chapters whose subject matter is divided according to the type of study—absorption, distribution, and excretion, permeability, turnover, path of intermediary reactions, skeletal metabolism, and study of red cells. Consequently, information relative to the application of a given isotope may be found in any one of several chapters. Besides studies with the radioactive isotopes, some work with deuterium is included. On the whole, the arrangement of the chapters into sections and subsections is good. However, Chapter VIII concerning turnover is practically identical with material published by the same author in "Advances in Enzymology," Vol. 6, 1948. The material relative to the turnover of C¹¹ and C¹⁴ labeled compounds is hardly satisfactory when considered apart from similar work involving C¹³. In fact, the consideration of tracer experiments separately from the general experimental background is probably a deplorable practice.

It appears to the writer that the author should have adopted a more critical attitude. Much of the material given prominence represents preliminary work in new fields and such work sometimes is presented almost side by side with newer material derived from well devised experiments from which opposite conclusions may be drawn. It would perhaps be of greater value if more attention were to be paid to the pitfalls that lie in the way of isotope users in particular of radioactive tracers, both in the setting up and in the interpretation of experiments, lest the new handmaid of science prove to be more in the nature of a harlot.

H. TARVER

Reagents for Qualitative Inorganic Analysis. *P. E. Van Nieuwenburg and J. Gilles.* xxii + 379 pages. Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y., 1948. Price, \$7.50.

This volume constitutes the second report of the international committee on new analytical reactions and reagents of the International Union of Chemistry. Originally published in French in 1945, this English version is not a literal translation, but involves a definite revision.

The larger number of reagents considered in the earlier report has been considerably reduced by application of the following criteria, which the authors list as "essential characteristics that ought to be possessed by a given reagent in order to make us recommend its use": sensitivity, selectivity, possibility of obtaining the reagent, and stability. On this basis a maximum of five reagents are considered per element, permitting the use of a moderate range of modern techniques. The cations of some sixty metals are considered, including the ammonium ion, and thirty anions, plus elementary chlorine, bromine, and iodine, and sulfur dioxide.

The treatment of a particular test normally includes the following material: reagent formulas and names, bibliography (references tabulated on pages 317 to 344), mechanism of reaction, details of test, sensitivity and selectivity, and reagent solutions used.

The work was distributed among a number of group leaders and assistants, so that an actual experimental checking of the accuracy of the description and the sensitivity of the test by itself and in the presence of many other metals could be made. Very little attempt was made to suggest a scheme of preliminary separations before the tests are applied, although a few hints are given for the treatment of qualitative groups.

The vast majority of the tests described involve the handling of very small amounts of material; a moderate number use as much as 5 ml. of solution. In the technical introduction it is explained, correctly, that the sensitivities of the tests apply to the particular procedures being used. The chemist must be on his guard against assuming that the same figure would apply if the test were carried out under significantly different conditions.

A short list of errata accompanies the book, dealing chiefly with corrections in spelling and English. The list is decidedly incomplete and in a number of cases minor questions of English practice might be raised.

Realizing the immense amount of work involved in actually checking the behavior of a large number of reagents with a large number of cations or anions in various combinations and under various other conditions, one must be grateful to these men for their work in this field. The results of their labors, and the references to the original articles, are conveniently assembled in the present volume. It will be very useful as a starting point for developing systematic schemes of analysis which may avoid many of the difficulties to be found in those at present available. The chemist facing problems of trace analysis in either simple or complex systems will also find much valuable information in its pages.

R. K. McALPINE

Introductory Quantitative Analysis. *Axel R. Olson, Edwin F. Orlemann, and Charles W. Koch.* viii + 299 pages. W. H. Freeman and Co., 549 Market St., San Francisco, Calif., 1948. Price, \$3.25.

The authors, members of the faculty of the University of California, have prepared a text for a short introductory course. They state their objective to be emphasis upon fundamental techniques and principles rather than a general survey of the entire field.

The theoretical material is clearly and concisely written and is distributed through the text so that a given discussion appears adjacent to the first laboratory exercise to which it is pertinent. Somewhat more stress is laid upon the underlying physical chemistry than in most texts of comparable length. Examples are three pages upon the drying of solids, twelve pages upon physical character and purity of precipitates, and twelve pages upon oxidation potentials. About 150 problems, most of them numerical and with answers, are provided. The selection seems adequate. Sample problems are clearly demonstrated, with a minimum of reliance upon formulas.

The laboratory exercises are standard, but limited in number. Gravimetric work (water in a hydrate, chloride, sulfate, iron) precedes volumetric (chloride by Fajans and Volhard processes, neutralization methods for acid and carbonate-bicarbonate mixture, iron by dichromate, calcium by permanganate, and

copper by thiosulfate). None of the exercises involves preliminary separations. A noteworthy feature is the freehand drawings illustrating technique, the work of Leonard W. Tregillus. However, students following Figure 8-3 would break many burets. The figures illustrating apparatus and all graphs in the book are also drawn freehand.

The reviewer's principal adverse criticism is that the student is likely to emerge from a course based upon this text with an inadequate picture of the field as a whole. While the authors have disclaimed any intent to present a general survey, one might wonder if the student, especially the nonchemist who takes no more work in the field, will be given an adequate appreciation of separations by the one-page discussion in the closing chapter, or of the many techniques recently acquired by the analytical chemist from the field of physical chemistry by the four pages in the same chapter devoted to this subject. The omission of bibliography and footnote references also seems unwise to this reviewer.

Nevertheless, the book is commended to the attention of any instructor offering a short beginning course in the field.

JOSEPH L. NEAL

Correspondence

SIR: In the article on "Separation and Microdetermination of Small Amounts of Aluminum" [ANAL. CHEM., 20, 1102 (1948)], it was stated in error that "the use of oxine as a precipitating agent for aluminum was first proposed by Berg." Although Berg was active in the development of applications for oxine, its use as an analytical reagent for aluminum was first proposed by F. L. Hahn [*Chem.-Ztg.*, 50, 754 (1926); *Z. angew. Chem.*, 39, 1198 (1926)]. Hahn also proposed the name "oxine" for the reagent.

Shell Development Co.
Emeryville, Calif.

THOMAS D. PARKS
LOUIS LYKKE

Conference on Applied Spectroscopy

THE Ninth Pittsburgh Conference on Applied Spectroscopy, sponsored by the Spectroscopy Society of Pittsburgh and the Department of Physics, University of Pittsburgh, was held February 18 and 19 at Mellon Institute, Pittsburgh, Pa. Abstracts of papers of particular interest to analytical chemists are given here.

Spectrochemical Analysis for Beryllium in Microquantities. E. C. BARNES, W. E. PIROS, T. C. BRYSON, AND G. W. WIENER, Westinghouse Electric Corp., East Pittsburgh, Pa.

A spectrochemical procedure has been developed, using a conventional direct current arc, for the quantitative determination of beryllium in amounts as low as 0.04 microgram per liter of urine. The sample is prepared by a phosphate precipitation to which aluminum is added to act as an internal standard. The amount of beryllium is determined by comparing the density of Be 2348.6 Å. to Al 2321.6 Å. The method has been successfully applied to tissue and air samples.

Spectrochemical Determination of Lithium in Gun Metal. H. LEVINE, Emission Spectroscopy and X-Ray Diffraction Section, Material Laboratory, New York Naval Shipyard, N. Y.

A spectrochemical method for the determination of trace amounts of lithium, used for the improvement of quality and soundness of cast gun metal, is described. Synthetic standards are made by adding varying amounts of lithium to solutions of the base alloy, which contains no lithium. Elements other than lithium are removed from the solutions so prepared. The copper,

tin, zinc, lead, nickel, and iron are separated by conventional methods, followed by final purification with the aid of the mercury cathode. Aliquots of these concentrated solution standards are impregnated in spectrographic carbon cups of special purity, and run in a 220-volt d.c. arc with unknown samples that have been similarly treated.

Based on such an initial standardization a suitable number of samples to cover the range desired is selected, machined into rod form, and used as secondary standards in subsequent production analyses of larger numbers of samples. In the rod form it is possible to take advantage of the greater over-all sensitivity and reproducibility of the a.c. arc method. Similar techniques may be applied to standardization of samples of other materials for spectrographic analysis, which are thereby made independent, to a large degree, of primary chemical analysis.

Standardization Work on Spectrographic Analysis of Low-Alloy Steel. S. GOLDSPIEL, Emission Spectroscopy and X-Ray Diffraction Section, Material Laboratory, New York Naval Shipyard, N. Y.

This communication reported on an evaluation of tentative methods of spectrographic analysis of low-alloy steels by the Material Laboratory, New York Naval Shipyard, as participant in the program of development of methods for the spectrographic analysis of steels under the cognizance of the Bureau of Ships Spectrographic Standardization Group. The investigation is being conducted so that "methods for different elements in any one type of material should involve as few distinct sets of conditions as possible in order to obtain higher speed of production." All methods described are based on the use of a Bausch & Lomb large Littrow spectrograph, and the University of Michigan interrupted spark excitation source, and are confined to rod samples.

The methods are described in accordance with the tentative form recommended by the administering laboratory to participants with special emphasis on accurate definition of excitation conditions. The estimate of precision is based on the correlation coefficient and standard errors of estimate of the regression equations using log per cent of constituent as the independent variable against log intensity ratio as the dependent variable, as justified by statistical considerations for low-alloy steels.

The work is based on 53 analyzed "standard" samples, run on 15 plates in groups of 5 plates, and comprising three sources of origin in order to provide a greater number of data for preliminary regression equations as well as information about dependence of such equations on the accuracy of chemical values assigned to standard samples as reflected by peculiarities of metallurgical preparation and chemical evaluation. The range of delta log *I* values for the respective standards was presented graphically on normal correlation contour plots for each line pair. Regression curves for seven elements, (with 2 line pairs for chromium, molybdenum, and nickel,) and a tabular summary of the analytical working curve data resulting from the methods were presented.

Evidence indicates that there exists a difference in the slopes of analytical working curves which depends upon the source of origin of the standard samples. Since plates are a significant source of variation, the significance of the sample source can best be studied by eliminating the effect of plates. An instrumentation adjustment to make possible the exposure of 53 samples in duplicate on a single plate was presented. Plans for further work were outlined.

Microwave Absorption Spectroscopy. DONALD K. COLES, Westinghouse Research Laboratories, East Pittsburgh, Pa.

Recent improvements in microwave spectroscopic apparatus were described. During the last year the threshold sensitivity for weak absorption lines has been improved by a factor of 10 or 100. Investigators are increasingly turning their attention from the simple molecules to asymmetric-top molecules, and even molecules with internal rotation. Methods for determining bond distances and potential barriers in molecules were outlined.

Anomalous Negative Peaks in Mass Spectra. A. G. SHARKEY, JR., AND R. A. FRIEDEL, U. S. Bureau of Mines, Synthetic Liquid Fuels Laboratories, Bruceton, Pa.

Negative peaks occurring two mass units lower than the positive ion peaks of carbon monoxide, carbon dioxide, nitrogen, and oxygen have been observed using a consolidated mass spectrometer. It appears possible for positive ions striking the metal exit slit surface to form negative ions which are then collected. Field conditions within the mass spectrometer tube are in the correct direction for this to occur.

The two most probable mechanisms of negative ion formation at metal surfaces by positive ions are:

1. Capture of two electrons by the positive ion [Arnot and Milligan, *Proc. Roy. Soc.*, A156, 538 (1936)].

2. Sputtering of occluded electronegative films [Sloane and Press, *Proc. Roy. Soc.*, A168, 284 (1938)].

In this experiment there was no evidence of a previous sample in the mass spectrometer tube giving rise to negative ions; this would tend to support the first theory of formation.

Negative nitrogen ions which Arnot and Beckett [*Proc. Roy. Soc.*, A168, 103 (1938)] were unable to observe were found. The ratio of negative to positive ions was about 4×10^{-4} for the four gases investigated. The values obtained by Arnot [*Proc. Roy. Soc.*, A158, 137 (1937)] vary from 10^{-3} to 10^{-5} for various gases.

Mass Spectrometer Analyses. C₅-C₈ Paraffin Isomers from Fischer-Tropsch Cobalt Catalyst Products. Carbon 13, Oxygen 18, and Deuterium. R. A. FRIEDEL AND A. G. SHARKEY, JR., U. S. Bureau of Mines, Synthetic Liquid Fuels Laboratories, Bruceton, Pa.

The C₅-C₈ paraffin isomers in a liquid product from Fischer-Tropsch cobalt catalyst have been analyzed. The major constituents are the straight-chain compounds. All the possible monomethyl derivatives were present; tests for more highly branched isomers were negative, though traces of these were not precluded.

Examples were given of mass spectrometer analyses of carbon 13 in methane, carbon monoxide, and carbon dioxide; and of oxygen in nitric oxide, nitrogen peroxide, carbon monoxide, carbon dioxide, and water, separately and in mixtures. Precision and accuracy of these determinations were discussed.

Simple and accurate analyses of deuterium in H₂O-HDO-D₂O mixtures have been carried out through reaction with CH₃MgI and analysis of the resultant CH₄-CH₃D mixture. Hydrogen deuteride, HD, has been prepared chemically with a purity of 99%. Accurate determination of its complete mass spectrum, in spite of interfering hydrogen impurity, has been carried out by means of diffusion measurements.

Spectrographic Analysis of Silica Refractories Using a Controlled Multisource Power Unit. A. J. HERDLE AND H. J. WOLTHORN, Ohio Works Chemical Laboratory, Carnegie-Illinois Steel Corp., Youngstown, Ohio.

A rapid method for the spectrographic analysis of silica refractories containing approximately 95% silica utilizes directly a sample of the refractory material, pulverized to pass through a 100-mesh sieve, for the determination of calcium, magnesium, titanium, aluminum, iron, sodium, and potassium, with the determination of silicon by difference.

The sample is placed in a center-post crater type carbon electrode and sparked with a high capacity overdamped condenser discharge using a pointed carbon counter electrode. Intensity ratios of selected analytical lines compared to a silicon line as internal standard are determined and the various concentrations read from analytical curves calibrated to read directly as the oxides of the elements determined.

Data obtained in determining the precision of the method were presented.

Applied Flame Photometry. C. L. WARING, Aluminum Research Laboratories, New Kensington, Pa.

Emission spectrometry has been applied to the analysis of various types of soluble materials through the use of the Beckman flame spectrophotometer, a monochromatic instrument. Methods are presented for the determination of lithium, potassium, sodium, calcium, magnesium, silicon, barium, manganese, indium, thallium, boron, and copper in materials related to the aluminum industry. These methods are applicable to samples as oxides, salts, solutions, and metals.

Flame photometry is similar to spectrographic arc and spark analysis, in that one element may depress or enhance the spectral emission of other elements. A knowledge of these effects is necessary for accurate determinations. Some of these effects were presented in connection with data on the accuracy of flame analysis.

The compilation of data for statistical treatment is in progress. Standard deviations were presented.

Extraneous Element Effects in the D. C. Arc. DONALD L. TIMMA, Ohio State University, Columbus, Ohio, AND WALLACE R. BRODE, National Bureau of Standards, Washington, D. C.

The effect of varying amounts of extraneous element upon the line intensity of different elements has been investigated. Slavin's

total energy method was used to make possible a more direct correlation than has been achieved using the internal standard method. The results of this study indicate that the effect of the extraneous element varies with the amount of extraneous element, but not in a simple linear fashion. The effect of an extraneous element on a group of lines of an element ending at the same energy level or beginning at the same energy level, is the same.

The experimental results show that the elements can be arranged in a series based on their interelement effects in the d.c. arc. An arrangement of the elements in a series based on their boiling points and excitation potentials is in agreement with that found experimentally.

Difficulties and Methods in the Infrared Analysis of Oxygenated Compounds. NORMAN D. COGGESHALL AND ELEANOR L. SAUER, Gulf Research and Development Co., Pittsburgh, Pa.

The increasing importance of liquid synthetic fuels has focused attention on the analysis of the oxygenated products which are by-products of the synthesis processes. The infrared absorption analysis of mixtures of oxygenated compounds is, in general, much more difficult than the analysis of hydrocarbons of the same molecular weight range. This is due to the existence of a number of intermolecular interaction phenomena which are operative in the liquid phase. One example of such interactions is the formation of hydrogen bonds, which results in the shifting and intensification of certain absorption maxima. Another example is in the disturbance of the keto-enol equilibria, which may depend upon composition of the sample and the presence of ionizable constituents. All these effects will, at times, render the direct application of Beer's law ineffective. Results of investigations of these phenomena and methods useful for circumventing particular difficulties were discussed. The high boiling points of simple alcohols are due to hydrogen bonding. When the concentration of the low molecular weight alcohols in a sample is small special methods must be used to avoid differential evaporation losses. Data and discussion were given of the analysis of samples for specific groupings in terms of moles per liter. Results of synthetic samples and other tests for the various analyses were presented.

Infrared Spectroscopy Aids the Drying Oil Chemist. F. J. HONN, D. D. BROWNING, AND I. I. BEZMAN, Mellon Institute, Pittsburgh, Pa.

Infrared spectroscopic measurements furnish means of following the many reactions occurring during drying oil autoxidation. The prominent absorption bands exhibited by oxidized drying oils have been identified, and the hydroxyl band has been studied in detail. A quantitative spectroscopic technique has been devised for analysis of drying oil-vinyl copolymers.

Presentation of Absorption Spectra Data. WALLACE R. BRODE, National Bureau of Standards, Washington, D. C.

The application of qualitative and quantitative methods of analysis as well as theoretical studies on molecular structure to absorption spectra data, in the same manner that these measurements are applied to emission spectra data, requires considerable development and coordination of effort to be effective. A survey was presented of the problem involved, the method of recording and describing effects, the notation systems, and general recommendations by various workers on the methods of graphical presentation.

The programs for the development of cooperative programs for the issuance of standard absorption spectra data at the National Bureau of Standards and other laboratories were discussed.

Applications of Ultraviolet Absorption Spectroscopy in the Study of the Chemical Nature of Coal Hydrogenation Products. RICHARD A. GLENN, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

A review was presented of the ways in which ultraviolet absorption spectra have been and are being used in the investigation of the chemical nature of the complex mixture of compounds obtained by the hydrogenation of coal. Selected data and results were illustrated with slides.

Preliminary Investigations and Techniques of Hollow Cathodes. K. B. ADAMS, Westinghouse Research Laboratory, East Pittsburgh, Pa.

A brief historical survey was given of the "hollow cathode" developed by Paschen in 1916. The refinements used today are nearly all attributed to Schuler and his students. Types of spectrum analysis that have been done with this source were

summarized. Most of the work has been done on hyperfine structure, as this is one of the few means of spectral excitation that give lines sharp enough for measurable results. There have been few applications of the hollow cathode as an analytical tool.

Several tubes used and a gas handling-circulating system were described. Examples were given of typical spectra photographed on a large B & L spectrograph showing halogens, selenium, etc.

Index for Identifying Positions of Spectrograms Projected on a Comparator. A. J. MITTELDORF AND J. P. CESTARO, National Lead Research Laboratories, Brooklyn, N. Y.

In spectrochemical analytical work, a number of spectrograms are generally photographed on one plate or strip of film. As commercial comparators have no means for identifying positions of the spectrograms, the operator must count from the first or last spectrogram to determine which spectrogram he is viewing. To facilitate identification of the spectrograms, a device has been designed and built which projects a number alongside of each spectrogram corresponding to its position on the film. Independent of the wave-length region projected, the operator can, at a glance, tell which spectrogram he is viewing. Although its principle seems adaptable to other comparators, the index has been built specifically for the A.R.L. instrument using a 35-mm. film carriage.

Analysis of Solids by the Mass Spectrometer. W. M. HICKAM, Westinghouse Research Laboratories, East Pittsburgh, Pa.

A furnace has been added to the mass spectrometer tube for vaporizing solid samples of known weight. The resulting molecular beam is subjected to electron bombardment. Ions formed are separated according to their mass to charge ratio by the general electromagnetic principle. The integral of the ion current with respect to time for a given m/e value is found to be proportional to the total amount of that element present in a particular sample. Applying this method to a study of impurities in copper, sensitivities of the order of a few parts per million are obtained for silver, arsenic, selenium, antimony, cadmium, and sulfur when using 2-mg. samples. The high vapor pressure of these elements compared to copper at the furnace temperature provides rapid vaporization and the resulting high sensitivity.

Recent Developments in Adapting Commercial Spectrographs for Use as Direct Reading Instruments. M. F. HASLER, Applied Research Laboratories, Glendale, Calif.

Intensive studies have been made concerning the limitations to be expected in applying direct reading receivers to commercial spectrographs. A proposed system allows good practical results to be obtained. Results obtained with this system in the analysis of low-alloy steels were discussed.

Effect of Hydroxyl Ions on the Ultraviolet Absorption Spectra of Substituted Phenols. NORMAN D. COGGESHALL AND ALVIN S. GLESSNER, JR., Gulf Research and Development Co., Pittsburgh, Pa.

When sodium hydroxide is added to an ethanol solution of any of the simple phenols there is a radical change in the ultraviolet absorption spectra. The absorption band ascribable to the phenyl ring is shifted to the red of the order of 18 millimicrons and intensified. This phenomenon has been investigated. It was tested for a series of other materials which provide hydroxyl ions to the solution, and for materials which add cations and anions of other types. The behavior of the shifted spectra as a function of temperature was determined. These tests indicated conclusively that the shifted spectra are those of the phenolate ions. The phenomenon was also investigated for a series of substituted phenols comprising unhindered, partially hindered, and hindered phenols. It was found that the action of the hydroxyl ions in producing ionization is dependent on the degree of steric hindrance present in the phenol molecule. Large groups on the ortho positions are very effective in hindering ionization. This has an important consequence in the consideration of the ionization processes, as it implies that close encounters between the phenol hydroxyl groups and other molecules or ions are necessary to produce ionization. An examination of the data shows that the transition energies for the hindered phenols are relatively greater than for the partially hindered phenols, which in turn are relatively greater than for the unhindered phenols. This result is interpreted in terms of the energy of polarization of the large ortho groups by the strong electric fields due to the accumulation of charge on the oxygen atom in the phenolate ion.

Adaptation of Beckman Spectrophotometer for Measuring Total Fluorescence and Fluorescent Spectra. J. J. MCGOVERN AND J. D. RODGERS, Mellon Institute, Pittsburgh, Pa.

A simple modification of the reflectance attachment unit of a Beckman spectrophotometer to permit the measuring of total relative fluorescence was described. The Beckman source, detection and measuring system is used, but the monochromator is bypassed and filters are used to define the exciting and emitted light. Some results obtained on fluorescent materials were presented.

An inexpensive readily constructed attachment for measuring fluorescent spectra with the Beckman spectrophotometer was also discussed. This unit is similar to the one described by Burdett and Jones (*J. Optical Soc. Am.*, July 1947). Several spectra obtained with it were shown.

Microchemical Symposium

THE Fourth Annual Microchemical Symposium, sponsored by the Metropolitan Microchemical Society of New York, was held February 25 and 26 at the American Museum of Natural History, New York, N. Y. Abstracts of some of the papers are presented below.

Radioactivity in Microanalysis. JOHN F. FLAGG, General Electric Co., Knolls Atomic Power Laboratory, Schenectady, N. Y.

The use of radioactivity and radioactive substances in microanalysis is of much potential importance. The general methods and techniques involved in such applications were reviewed, and specific cases discussed in which applications have been made in analytical problems.

Radioactive materials suitable for use as tracers in analytical work may be obtained from natural sources, or produced by nuclear bombardment. The first source furnishes isotopes of the heavy elements, while by the second method isotopes of any element may be produced. The manner in which an isotope is produced may be influenced by the use to which it is to be put, in which factors such as radiochemical purity and specific activity are important.

Methods for measuring radioactive materials are now well standardized, and a variety of reliable commercial equipment is available without restriction for isotope work.

The applications discussed included the electrodeposition method, the adsorption method, the activation method, and the isotope dilution method.

In the electrodeposition method, the deposition potential of a metallic element is determined by measuring its radioactivity on an electrode. From the deposition potential it is possible to approximate the single electrode potential and thus, by the Nernst equation, the concentration of the ion in solution. The method has been applied to dilute solutions of bismuth and polonium.

The adsorption method depends on the measurement of extremely small amounts of ions adsorbed on an adsorbant such as ferric hydroxide. The relationship between amount adsorbed and concentration is defined by an empirical equation from which concentrations in unknown cases may be calculated. The method has been used in the analysis of dilute barium solutions.

The activation method depends on the conversion of trace metallic impurities to radioactive isotopes by exposure to neutrons or other bombarding particles. The amount of radioactive material formed by the bombardment may be measured, and thus indirectly the amount of trace impurity initially present.

The isotope dilution method involves the addition of a small, known amount of tagged material to a sample in which a larger, unknown amount of the same material is to be determined. After thorough mixing of tagged and inactive components a portion of the substance sought is separated in pure form and its activity determined. From the weight isolated, and its radioactivity content, it becomes possible to calculate the amount of the unknown material initially present in the sample. Many applications of this method have been made.

Determination of Traces of Elements. CLEMENT J. RODDEN, National Bureau of Standards, Washington, D. C.

The great importance of traces of elements has only recently been realized. The metallurgists and the electroplaters are interested, and they are of great concern to those working in nuclear chain reactions. The determination of traces of elements deals with those present in the range of fractions of 1% to fractions of one part in a million. As is seen from the magnitude of these

traces, the usual laboratory procedures and techniques are inadequate and must be revamped or new ones devised.

Spectrographic methods are extremely sensitive and can be used with modifications. An example of such modifications is the "carrier-distillations" technique. Oftentimes, as with the rare earths determinations, the spectrograph cannot be used unless chemical separations are first made. Many chemical methods of separating and concentrating traces have been devised and the analyst usually has a choice of methods.

The best known of the chemical methods for trace determinations is the color produced by complexes or compounds formed on the addition of an inorganic or an organic compound. These may be extremely sensitive when the color is measured in monochromatic light. If a fluorescence is produced instead of a color it can be measured in the same manner using the proper filter. This is the most sensitive method known for the determination of uranium. Another chemical method often employed by the trace analyst is to effect a separation of the ions to be determined from those initially present by coprecipitation using an added carrier ion known to be inactive in the final determination. Much work on carrier ions was done by the Manhattan Project. One further method of separation, long known but little used, has been that of organic solvent extraction. The effect of pH and added salts is a vast unexplored field with solvent extractions.

Physicochemical methods may find employment in trace determinations. One such method, recently attracting attention, is volatilization. Low pressure gasometric methods may find an important place in the analyses of traces of gaseous elements in metals. Another physicochemical method is that of electrolysis using the mercury cathode. This method combined with the distillation of the mercury is a sensitive way for separating and concentrating trace elements, which may then be determined using polarographic or colorimetric procedures. Another sensitive method is the determination of radioactive elements using the Geiger-Müller counter apparatus. This method is sensitive enough to determine uranium or thorium in the range of 0.001%.

A method or methods can be devised for each problem, but each problem is a challenge to the ingenuity of the trace analyst.

Instrumentation in Microanalysis. RALPH H. MÜLLER, New York University, Washington Square College of Arts and Science, New York, N. Y.

Although many of the instrumental methods of analysis which are widely used today can detect and estimate very small amounts of substances and often handle very small samples, another phase of instrumentation can contribute to the advance of microchemistry. Some of these approaches, currently under way at New York University, were described.

One of these deals with the instrumentation of paper chromatography. Müller and Clegg have shown that the diffusion of colored mixtures through paper media can be followed photoelectrically and recorded automatically, and that the kinetics as well as quantitative separation of microgram quantities can be followed with great speed and precision. The method is inherently capable of extension to the ultraviolet and therefore to colorless substances.

A complementary study with Stevens measures progressive changes in electrolytic conductance on paper-strip chromatograms and records these changes automatically. It is primarily suited for those systems, organic or inorganic, which exhibit appreciable conductance. Instrumental designs for an approach to the automatic weighing of individual drops as they emanate from conventional chromatographic columns are being tested by Le Strange.

Some new methods for refractive index and dispersion measurements are being studied by Rabinowitz and Frachtman; the former is concerned with the high-speed indication of n at eight different wave lengths and presentation on a cathode ray tube. Simultaneous pips are presented on the screen from a reference substance, affording differential index and dispersion values. The other study is concerned with the recording of small changes of refractive index. Both methods are adaptable to relatively small samples.

Some instrumental applications to micro melting points and molecular weights by the cryoscopic method are under investigation by Zenchelsky and the speaker. An optical-electronic servomechanism has been developed which will cause a sample to keep the micro hot stage hovering within a fraction of a degree at the true melting point. Another technique automatically measures the temperature increment in a cryoscopic molecular weight system and by a simple electrical network computer furnishes molecular weight directly.

Other electroanalytical techniques which are adaptable to the micro range were described.

The Ultracentrifuge. E. G. PICKELS, Specialized Instruments Corp., Belmont, Calif.

The molecular weight or particle size of macromolecules in quantities as low as 1 mg. of solute can be determined by combining the sedimentation rate, as measured optically in an ultracentrifuge, with the diffusion constant according to the methods of Svedberg and his associates. Or the rate may be determined by sampling the material at the end of the ultracentrifugation; the only limitation in the minimum amount of material required is that set by the sensitivity with which some property of the material can be measured. The so-called sedimentation velocity method based on the detection and measurement of sedimenting boundaries is particularly suited to the resolution and study of mixtures and permits the determination of molecular weights down to about 10,000, the principal limitation being set by the Brownian movement of the molecules, which progressively decreases the definition of the sedimenting boundary. The equilibrium method in which the sedimentation and diffusion are balanced within the centrifuge permits the determination of molecular weights considerably below 1000 in the case of monodispersed materials. Solvation, electrical charge on the particles, and interaction between the sedimenting particles, particularly as reflected in the effect on the viscosity of the solution, introduced some complication in the interpretation of results, but techniques believed to be adequate for dealing with these factors have been perfected.

Most ultracentrifuge rotors are now suspended from a flexible steel shaft to permit self-balancing and rotate in an evacuated chamber to eliminate air resistance and heating which would cause convective disturbances within the material under study. Although most vacuum centrifuges have in the past been air-driven, the present commercial model is electrically driven through a high-speed gear train. Its operation is almost completely automatic. Speeds with 7-inch rotors up to 60,000 r.p.m., produce average centrifugal forces up to 260,000 times gravity in the fluid column. Interchangeable preparative rotors as well as analytical rotors with transparent cells for optical work may be used. Rotor temperature rises about 1° per hour. For low temperature operation the inner wall of the vacuum chamber may be refrigerated.

Photographs obtained with a Philpot-Svensson refractive index method of the cylindrical lens type show a peak corresponding to each sedimenting boundary, the size of the peak being related to the concentration of the particular component.

The Analyst's Calendar

Analytical Group of North Jersey Section

The fourth meeting of the Analytical Group of the North Jersey Section, AMERICAN CHEMICAL SOCIETY, will take place April 13 at 8 P.M. in the Public Service Auditorium, Newark, N. J. Officers for 1949-50 will be elected.

The speaker of the evening, Daniel Norman, New England Spectrochemical Laboratories, will discuss chemical analysis of organic compounds by their emission band spectra, following an informal dinner at 6:15 P.M., Newark Athletic Club. Reservations should be made with Al Steyermark, Hoffmann-LaRoche, Inc., Nutley, N. J., before April 7.

Crystallographic Society of America. University of Michigan, Ann Arbor, Mich., April 7 to 9, 1949.

Instrument Society of America. Royal York Hotel, Toronto, Canada, May 12 and 13, 1949.

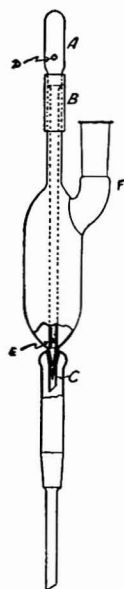
Second Annual Summer Symposium on Analytical Chemistry. Wesleyan University, Middletown, Conn., June 24 and 25, 1949.

Fourth Instrument Conference and Exhibit. Municipal Auditorium, St. Louis, Mo., September 12 to 16, 1949.

AIDS FOR THE ANALYST

Dropping Funnel without Stopcock. J. P. E. Human and John A. Mills, University of Adelaide, Adelaide S. A., Australia.

THE conventional type of dropping funnel with a bored-plug stopcock has a number of disadvantages, and funnels without external taps have been described [Hershberg, *Organic Syntheses*, Coll. Vol. II, 129 (1943); Kobe, *IND. ENG. CHEM., ANAL. ED.*, 16, 641 (1944)]. The funnel shown in the figure, with what is essentially a glass needle valve, gives a flexibility and ease of control very suitable for general laboratory use.



Plunger A, made of sealed-off glass tubing, fits snugly in a guide tube and has its head enlarged somewhat so that it may be held firmly in any position by means of the tightly fitting rubber sleeve, B, which is lightly lubricated with glycerol or silicone grease. The tip of the plunger is drawn off accurately and ground into the conical jet, C, which is sealed into the base of the funnel. If the jet is correctly aligned and ground, the plunger should give a vacuum-tight seal when pushed in. It is convenient to have the top opening of the funnel offset as at F.

A regulated flow of liquid is obtained by loosening the plunger in its socket and withdrawing it slightly. If a very constant rate of flow is needed, the funnel may be adapted to the design of Ashburn and Frank [*IND. ENG. CHEM., ANAL. ED.*, 16, 418 (1944)] by having two holes, D and E, in the top and just above the tip, respectively. Jet C should be longer (2 to 3 cm.) in this case to ensure sufficient head of liquid to cause the device to function properly.

Funnels of this type have several advantages: The rate of flow is continuously variable over a wide range from 1 or 2 drops per minute upwards; there is no risk of the contents being contaminated with lubricant, nor of leakage when using such reagents as liquid bromine. In addition, the funnel lends itself to easy warming—for example, by encasing in a steam jacket if it should be necessary to keep the contents hot.

The dimensions of the funnel can vary considerably: the needle valves are usually made of tubing about 6 mm. in outside diameter for the plunger and the jet has a diameter of about 3 mm. with an orifice about 1 mm. at the tip.

Holder for Dropping Mercury Electrode. W. E. Allsopp, The Cleveland Twist Drill Company, Cleveland, Ohio.

ALTHOUGH many commercial polarographic accessories are available, no device is made for holding the capillary electrode in a vertical position to ensure reproducible drop rates [Müller, O. H., *J. Chem. Education*, 18, 65 (1941)]. The device described by Lykken [Lykken, Pompeo, and Weaver, *IND. ENG. CHEM., ANAL. ED.*, 17, 728 (1945)] with a special water bath to hold the electrode and cell assembly, seems complicated and expensive to construct.

The holder described below is easily constructed and convenient to use. Its flexibility permits ready introduction of the cell into the usual type of water bath and subsequent adjustment of the electrode.

Figure 1 is an isometric drawing of the unit.

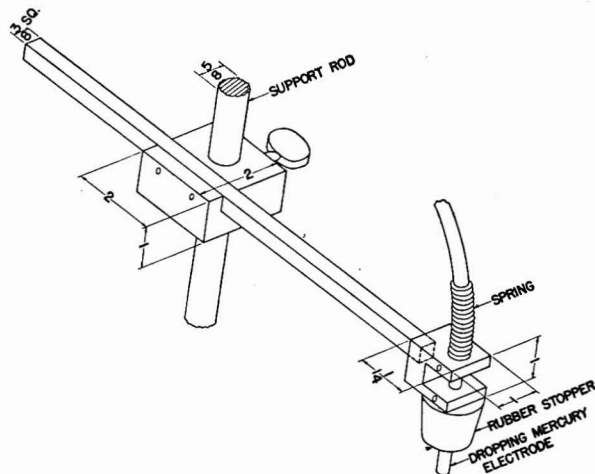


Figure 1. Electrode Holder

The spring used to prevent sharp bends in the rubber tubing was taken from an electrical appliance cord. The level shown in Figure 2 is a 4-inch machinist's level manufactured by the Stanley Tool Company.

The cell is placed in the water bath while the electrode is in a raised position. The electrode holder is then lowered to a predetermined mark on the ringstand support bar, thus immersing the capillary in the sample. The cell is then adjusted to a snug fit around the rubber stopper, which has a groove along one side to permit escape of the inert gas used to sweep oxygen from the solution. Use of the machinist's level ensures the horizontal position of the supporting arm.

ACKNOWLEDGMENT

The author is deeply indebted to W. L. Emerson, chief chemist, and J. V. Emmons, chief metallurgist, for their helpful interest, to G. H. Seaver for the preparation of the photographs, and to V. R. Damerell of Western Reserve University for his advice during the preparation of this paper.

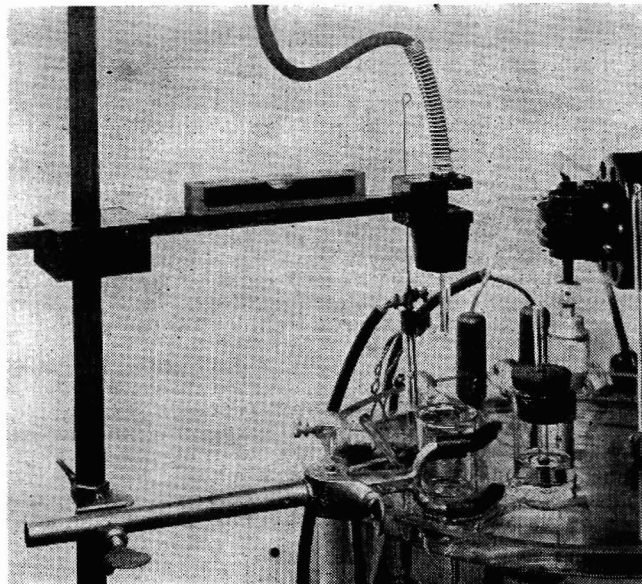


Figure 2. Electrode Holder